REVISION AND REFINEMENT OF THE CRYSTAL STRUCTURE OF PHARMACOSIDERITE

by

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Table of Contents

List of Figures

Figure

List of Tables

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Abstract

Pharmacosiderite is a hydrated iron arsenate mineral. A crystal structure for this compound was proposed by J. Zemann in 1948 based on the model of Hägele and Machatschki for the alumopharmacosiderite. The chemical formula proposed by Zemann was $[Fe_4(OH)_4(AsO_4)]K.(6\text{-}7)H_2O$ with a cubic cell with a = 7.93 Å, obtained from rotation photographs.

Both a spectrochemical analysis of the sample used for this work, and the results from a Fourier refinement of Zemann's structure, showed no potassium, so the formula of our material is $[Fe_4(OH)_4(AsO_4)_3]^{-1}(6\text{-}7)H_2O$. A cubic cell with a = 7.99 Å was deduced from precession photographs. The cell constant determined from measurements on precision back-reflection Weissenberg photographs, and adjusted by least-squares refinement, gave a final value of a = 7.9818 ± 0.0005 Å. The space group is $P\bar{4}3m$.

The structure determined here, essentially equivalent to Zemann's structure, consists of chains of AsO_4 tetrahedra linked to complexes of 4 $Fe(OH)_3O_3$ octahedra, each of the oxygen atoms of the tetrahedron being shared by the corner of an Fe octahedron. An Fe atom has three AsO_4 tetrahedra and three other Fe octahedra as neighbors. Each octahedron shares one edge formed by 2 OH radicals with each of the three other octahedra of the group. The distribution of the water molecules in the channels of the structure is the main difference between the structure proposed here and Zemann's structure.

Starting with Zemann's coordinates, the discrepancy factor, R, changed from 26.1% to 12.3% after three cycles of Fourier refinement and seven cycles of least-squares refinement.

Thesis Supervisor: Martin J. Buerger

Title: Institute Professor, Professor of Mineralogy and Crystallography

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Introduction

Pharmacosiderite is a hydrated iron arsenate mineral which was first described by Proust[1] in 1790. Since then, many chemical formulas have been assigned to this compound. Berzelius' chemical analysis[2] in 1824 suggested the composition $Fe_8As_6O_{21}.15H_2O$. Seventy-six years later Hartley[3] made new analyses and proposed the formula $2FeAsO_4.Fe(O,K)_3.5H_2O$. However, in 1928 Heide[4] reported that the potassium, instead of being a substituent of the hydrogen should take a place in the channels of the structure together with the zeolitic water.

The first serious attempt to establish the crystal structure of pharmacosiderite, together with its real chemical formula, was made in 1937 by Hägele and Machatschki[5]. They succeeded in synthesizing an Al analog of this compound as judged by the similarity of crystal shape, cell constants and general composition. Using powder photographs, they determined an isometric cell for both compounds and suggested space group $P\bar{4}3m$ as the symmetry. For their unit cell and measured densities, the cell should contain $1\frac{1}{2}$ of Hartley's formulas. In consequence they suggested that the new formulas $Al_5(AsO_4)_3(OH)_6.(6\text{-}8)H_2O$ and $Fe_5(AsO_4)_3(OH)_6.(6\text{-}8)H_2O$ should be accepted for alumopharmacosiderite and pharmacosiderite respectively. A structure based on these new formulas was also proposed by them; this structure consisted of a framework of AsO_4 tetrahedra located on the center of the cell edges, linked to groups of 5Fe octahedra located at the cell's corners.

The structure proposed by Hägele and Machatschki for alumopharmacosiderite and pharmacosiderite was re-examined in 1948 by Zemann[6, 7] with special regard to the iron compound. He confirmed the space group and obtained a similar value for the edge of the unit cell. However, he found poor agreement between computed and observed

intensities for Hagele's and Machatschki's structure and for several alternative models. This led him to the conclusion that a reinterpretation of the chemical analyses was necessary, and he showed that Hartley's analyses could be represented by the formula $[Fe_4(OH)_4(AsO_4)_3]K.(6\text{-}7)H_2O$. A structure based on this formula and on Hägele's and Machatschki's model gave a much better agreement between calculated and observed intensities. Table 1 gives a comparison of the Zemann's and the Hägele and Machatschki structure of pharmacosiderite showing the equipoints of the space group $P\bar{4}3m$ occupied on each of them.

Zemann's structure for pharmacosiderite has been generally accepted as essentially correct, and this structure was assigned to a series of alkali germanate compounds studied from 1953-1956 by Nowotny and Wittman[8, 9, 10, 11]. However, a detailed revision and refinement of this structure seemed desirable.

A sample of pharmacosiderite from Cornwall, England, was kindly provided by Professor Clifford Frondel of Harvard University to be used in the present investigation. The crystals, of emerald-green colour, showed a cubic habit with diagonally striated faces; the [001] cleavage was imperfect to good.

Table 1

Comparison of the structures for pharmacosiderite proposed by Hägele and Machatschki and by Zemann

Hägele and Machatschki	Zemann
5Fe(or 5Al) in 1(a) + 4(e)	4Fe in 4(e)
3As in 3(c)	3As in 3(c)
12O in 12(i)	12O in 12(i)
6(OH) in 6(f)	4(OH) in 4(e)
H_2O molecules in the channels of the structure, positions not specified.	4(H_2O) in 4(e) 3(H_2O) in 3(c)

Cell

Hägele and Machatschki's studies of pharmacosiderite and synthetic alumopharmacosiderite[5] were based on a cubic cell for both compounds with lattice constants of 7.96 Å and 7.77 Å respectively, obtained from powder photographs. Their results were confirmed later by Zemann[7] who determined lattice constants of 7.93 Å and 7.76 Å for pharmacosiderite from Cornwall (England) and synthetic alumopharmacosiderite respectively. These results were obtained from rotation photographs taken with Fe and Cu radiations.

For this work, a preliminary determination of the cell constant was made by means of precession photographs. Zero, first and second-level a-axis and a zero-level [110]-axis precession[12] photographs taken with Mo radiation, rendered an $\underline{a}$ value of 7.99 Å. A refined value for $\underline{a}$ was obtained using the data from a precision back-reflection Weissenberg photograph taken with Fe radiation, according to the method described by Buerger[13]. These data were used as input for the LCLSQ3 program written by Burnham[14] for the IBM 7094 computer and submitted to 3 cycles of least-squares refinement. The final value of $\underline{a}$ was 7.9818 ±0.0005 Å. Table 2 gives a resume of the values of pharamcosiderite's $\underline{a}$ constant as obtained by the different authors.

Table 2

Values of the lattice constant a of pharmacosiderite

Author	Method	a
Hägele and Machatschki	Powder photographs	7.96 Å
Zemann	Rotation photographs	7.93 Å
	Precession photographs	7.99 Å
This work	Back-reflection Weissenberg photograph + least squares refinement	7.9816 ± 0.0005 Å

Space group

Hägele and Machatschki[5] and Zemann[7] assigned the structure of pharmacosiderite to space group $T_d^1 = P\bar{4}3m$. This result was obtained on the basis of morphology observations that suggested the macrosymmetry $T_d = \bar{4}3m$, the lack of systematic absences in the photographs, the Laue symmetry of $O_h = m3m$, and a primitive cell.

This symmetry was confirmed in the present work by means of precession photographs. Of the three possible space groups P43, Pm3m and $P\bar{4}3m$ compatible with the photographs, the last one was chosen in agreement with the arguments of previous investigators.

It must be noted, however, that Hocart[15] reported that observations of pharmacosiderite crystals under polarized light showed that the crystals are pseudo cubic, of monoclinic symmetry, and are twinned on the (110) pseudosymmetry planes. Nevertheless, Zemann specifically looked for intermediate spots in the photographs which could be interpreted as doubling of the cell edge, or twinning, and he was unable to find them.

Figure 1 shows the symmetry elements[16] of the space group $P\bar{4}3m$. Coordinates for general and special positions[17] are shown in Table 3.

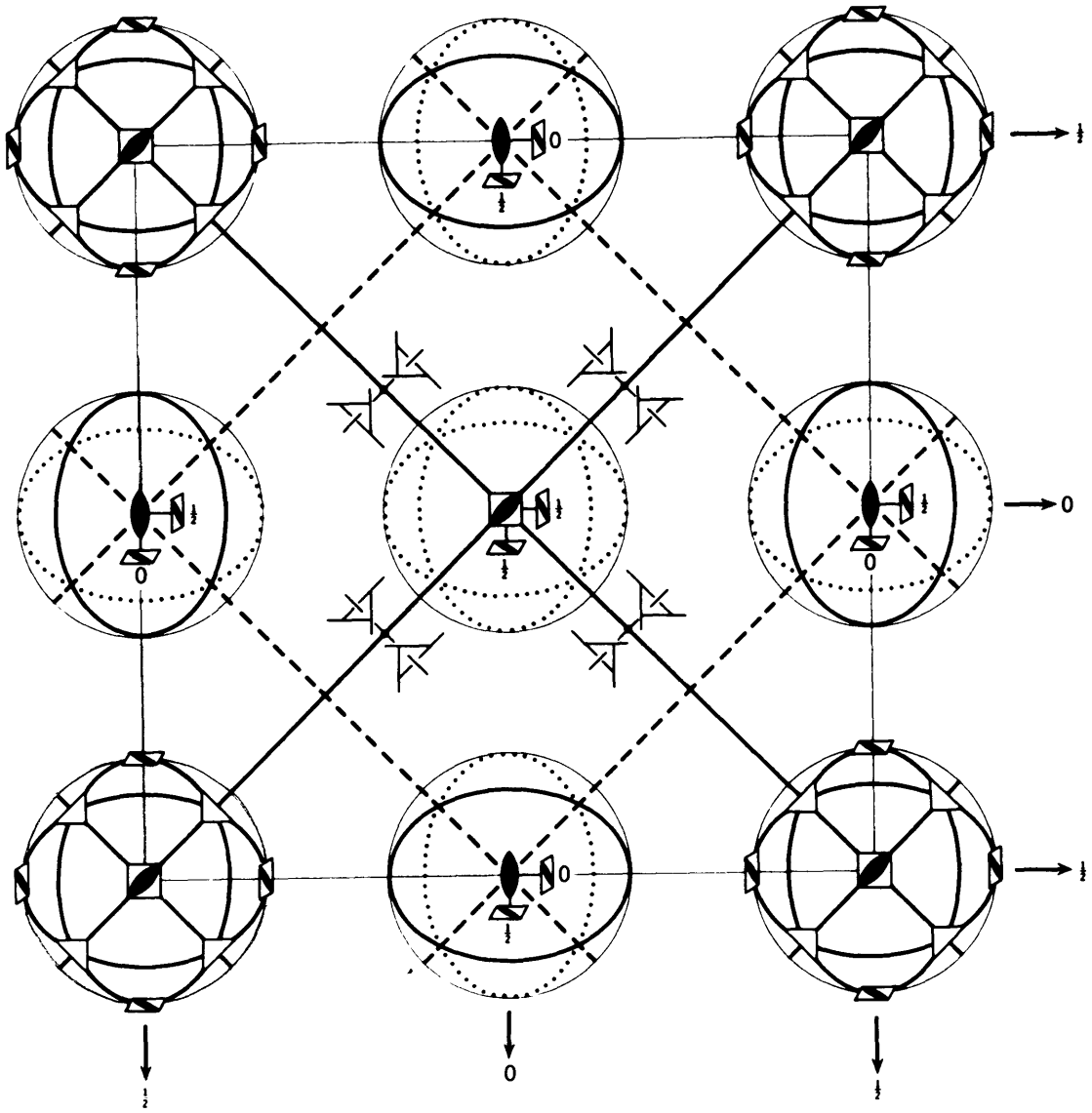

Fig. 1. Space group $P\bar{4}3m$

(After M.J. Buerger [16].

Table 3

General and special positions for the
space group $P\bar{4}3m$ with the origin at $\bar{4}3m$

Rank and designation of equivalent position	Point symmetry	Coordinates of representative points
24 j	1	x y z
12 i	m	x x z
12 h	2	x $\frac{1}{2}$ 0
6 g	mm	x $\frac{1}{2}$ $\frac{1}{2}$
6 f	mm	x 0 0
4 e	3m	x x x
3 d	$\bar{4}2m$	$\frac{1}{2}$ 0 0
3 c	$\bar{4}2m$	0 $\frac{1}{2}$ $\frac{1}{2}$
1 b	$\bar{4}3m$	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$
1 a	$\bar{4}3m$	0 0 0

Number of formulas per cell and specific gravity

The number $\underline{n}$ of formulas per cell for Zemann's chemical formula $[Fe_4(OH)_4(AsO_4)_3]K.7H_2O$, was computed using the relation $n = \frac{V\rho_o N}{A}$, where:

$V = 508.475 \times 10^{-24}$ cm^3 (with a = 7.9816 Å)

$\rho_o = 2.797$ g/cm^3 [18]

$N = 0.602 \times 10^{24}$ (Avogadro Number)

A = formula weight

Since, as shown in Table 4, the different chemical analyses did not agree in the presence of the K ion, the same calculation was repeated for the ideal formula $Fe_4(OH_4)(AsO_4)_3 \cdot 7H_2O$. The agreement between ρ_o and ρ_c was also tested for 6 water molecules on both formulas proposed. The values obtained for n and ρ_c are shown in Table 5.

Table 4

Chemical analyses of pharmacosiderite

	Hartley			Ideal (Zemann)	Ideal
	I	II	III	$[Fe_4(OH)_4(AsO_4)_3]K.7H_2O$	$Fe_4(OH)_4(AsO_4)_3.7H_2O$
Fe_2O_3	39.29	38.81	37.58	36.5	38.24
As_2O_5+ P_2O_5	39.57	38.91	38.36	39.5	41.27
H_2O	19.63	19.63	18.85	18.6	20.49
K_2O	-	-	4.54	5.4	-
	98.49%	97.35%	99.33%	100.0%	100.00%

Table 5

Number of formulas (n) and calculated density (ρ_c) for pharmacosiderite

		n	ρ_c
$[Fe_4(OH)_4(AsO_4)_3]K$ with	$6H_2O$	1.001	2.793
	$7H_2O$	0.980	2.853
$[Fe_4(OH)_4(AsO_4)_3]$ with	$6H_2O$	1.049	2.667
	$7H_2O$	1.026	2.725

Intensity measurements

A single crystal of dimensions 0.126 x 0.140 x 0.164 mm was used for the intensity measurements. It was first oriented optically and then by means of precession photographs. Before starting the collection of the intensities the correct orientation of the crystal on the diffractometer was checked according to Wuensch's method[19] by recording on a small film the reflections 400, $\bar{4}00$, 040, and $0\bar{4}0$.

The three-dimensional set of intensities was obtained with a single-crystal diffractometer based on equi-inclination geometry. An argon-filled proportional counter was employed as detector associated with Norelco electronic equipment which included pulse-height analysis circuitry. Cu radiation with Ni filter was used, and the generator was stabilized at 35 kV and 15 mA. The equi-inclination angles Υ and φ and the angle θ were determined using the DFSET 4 program written by Prewitt[20, 21].

A total of 121 reflections were recorded, corresponding to levels 0 to 9. In order to keep the measurements within the range of linearity of the counter the 30 strongest reflections, which presented a peak intensity larger than 650 count/sec, were measured using an aluminum sheet 0.211 mm thick as an absorber. The transmission factor of the Al sheet was obtained approximately by measuring the intensity with and without the absorber in 10 moderately strong reflections. An exact determination of the transmission factor was not intended; instead, in the least-squares refinement, two different scale factors were assigned to the reflections measured with the absorber and without it.

Counter-intensity data for each reflection consisted of the scan count (i.e., total number of counts while the crystal was rotated through the maxima, from a position $\varphi_1 > \varphi$ (hkl)) and fixed-time

background counts for the positions φ_1 and φ_2.

The integrated intensities were computed using the relationship:

$$I = s \left(E - \frac{B_1 + B_2}{2 T_b} \cdot T_e \right)$$

where:

I = integrated intensity

E = scan counts

B_1 = background counts at the position φ_1

B_2 = background counts at the position φ_2

T_b = fixed time of background counting

T_e = peak counting time

s = scale-factor.

Integrated intensities and Lorentz-polarization correction were computed with the FINTE 2 program written by Onken[22].

Absorption correction

Since the crystal used on intensity measurements had the shape of a parallelopiped, the transmission factor for each integrated intensity was computed by means of the GNABS program written by Burnham[14]. This program makes a general absorption correction for the equi-inclination Weissenberg geometry for a crystal with plane faces (non-special shape) provided no reentrant angles are present. The computed linear absorption factor μ for this crystal and for the CuKα radiation was 315 cm^{-1}.

Revision and refinement of Zemann's structure

Zemann[7] proposed a structure for pharmacosiderite based on the model of Hägele and Machatschki[5] for the alumo-pharmacosiderite. The atomic coordinates for this model are given in Table 6. To test the correctness of Zemann's structure, his atomic coordinates (which did not include positions for the K ions) together with half-ionized f values[23] for Fe, As and O, and individual isotropic temperature factors, were submitted to least-squares refinement. The refinement was performed on an IBM 7094 computer, and the SFLSQ 3 program written by Prewitt[21] was used. The initial values of the isotropic temperature factors in $Å^2$ units were 0.5 for As, 0.5 for Fe, and 0.6 for oxygen. Two scale factors were included in the calculation (which distinguished between reflections measured with and without the Al abosrber) and were the only parameters allowed to vary during the first 2 cycles of refinement. No rejection test was included and all reflections were assigned a unit weight.

The weighted R factor for Zemann's structure of pharmacosiderite without a K ion was at the end of these two cycles of refinement 26.1%, the discrepancy factor R being defined as:

$$\text{unweighted R} = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$\text{weighted r.m.s R} = \left[\frac{\Sigma\omega(|F_o| - |F_c|)^2}{\Sigma\omega F_o^2}\right]^{\frac{1}{2}}$$

In order to locate the position of the K ion that Zemann predicted should be placed in the channels of the structure, a three-dimensional electron-density function $\rho_1(xyz)$ and a three-dimensional difference synthesis map $\Delta\rho_1(xyz)$ were computed using the MIFR 2

Table 6

Zemann's structural data for pharmacosiderite

Atom	Equipoint	Symmetry	Coordinates	Coordinate values
As	3d	42m	$\frac{1}{2}00$	
Fe	4e	3 m	xxx	x = 0.131
OH	4e	3m	xxx	x = 0.875
O	12i	m	xxz	x = 0.125 z = 0.375
H_2O (I)	4e	3m	xxx	x = 0.653
H_2O (II)	3c	42m	$0\frac{1}{2}\frac{1}{2}$	

program[21]. The signs of the structure-factor calculation for which R = 26.1% were used in combination with the $|F_o|$ values.

Both the electron-density map and the difference-synthesis map agreed on two interesting results:

(a) There was no peak which could be identified with the K ion.

(b) There was no atom in the position assigned by Zemann to the molecule H_2O (II).

At this stage, a sample of pharmacosiderite was sent to the Cabot Spectrochemistry Laboratory for a spectrochemical analysis in order to test the presence of either K or Na ions. This analysis showed only traces of K and Na; therefore, the formula for the compound appears to be $[Fe_4(OH)_4AsO_4)_3]^{-1}$. $(6\text{-}7)H_2O$.

In order to have a new conservative start, a three-dimensional electron-density function ρ_2 based on the signs of the As and Fe atoms only was calculated. This electron-density map showed, in addition to the expected peaks of Fe and As, peaks near the locations predicted by Zemann for the O, OH and H_2O (I). These positions, together with those of Fe and As, were submitted to a structure-factor calculation, and the signs determined in this way were used to form a new three-dimensional electron-density map $\rho(xyz)$. This showed a new maximum at 0.2, 0.5, 0.5 having a height of about one-third the height of the oxygen peak. This equipoint, of symmetry mm, corresponds to the special position 6g. Since, according to the chemical formula, we need to put three water molecules in this position, H_2O (II) must be statistically distributed, with multiplicity $\frac{1}{2}$, at this location.

When the atomic coordinates obtained from ρ_3 were submitted for a structure-factor calculation, a weighted R of 21.8% was obtained. Four cycles of refinement, varying atomic coordinates and scale factors, gave an R value of 16.6%, and three additional cycles allowing also the isotropic temperature coefficients to vary, yielded a final

R value of 12.3%.

The signs from the last structure-factor calculation were used to compute a final three-dimensional electron-density function and a three-dimensional difference map. The atomic coordinates and temperature coefficients, corresponding to the weighted R of 12.3%, are listed in Table 7. A composite of sections from the final electron-density function which contain maxima is shown in Fig. 2.

Description and discussion of the structure

The final arrangement of atoms in the structure corresponds basically to the structure given by Zemann[7]. AsO_4 tetrahedra and complexes of four $Fe(OH)_3O_3$ octahedra (surrounding the origin) form chains along the cell edges. The As of each AsO_4 tetrahedron is located in the center of a cell's edge, each of the oxygen atoms of the tetrahedron being shared by the corner of an Fe octahedron. An Fe atom has three AsO_4 tetrahedra and three other Fe octahedra as neighbours. Each $Fe(OH)_3O_3$ octahedron shares one edge formed by two OH radicals with each of the three other octahedra of the group (Fig. 3). The four H_2O (I) water molecules are located in the special position x x x with x = 0.10 instead of x = 0 as given by Zemann. The large channels are filled with water molecules in the way proposed by Zemann who also thought that these channels could include, besides positive ions, possibly K^+, Na^+ or Fe^{+++}.

It is useful to compare this structure with the structure of the series of alkali germanates $M_3HGe_7O_{16}\cdot 4H_2O$, where M stands for Li, Na, K, NH_4, Rb, Cs, Ag or Tl, given by Nowotny and Wittmann[8, 9, 10]. They assigned to these compounds a structure similar to Zemann's pharmacosiderite. Three of the seven Ge

Table 7

Final coordinates for the pharmacosiderite structure

Atom		Zemann	This work
As	x	$\frac{1}{2}$	$\frac{1}{2}$
	y	0	0
	z	0	0
	B	-	2.07
Fe	x	0.131	0.142 ± 0.001
	y	0.131	0.142 ± 0.001
	z	0.131	0.142 ± 0.001
	B	-	1.44
OH	x	0.875	0.890 ± 0.006
	y	0.875	0.890 ± 0.006
	z	0.875	0.890 ± 0.006
	B	-	4.24
O	x	0.125	0.124 ± 0.003
	y	0.125	0.124 ± 0.003
	z	0.375	0.387 ± 0.004
	B	-	1.99
$H_2O(I)$	x	0.653	0.683 ± 0.008
	y	0.653	0.683 ± 0.008
	z	0.653	0.683 ± 0.008
	B	-	9.99
$H_2O(II)$	x	0	0.10 ± 0.02
	y	$\frac{1}{2}$	$\frac{1}{2}$
	z	$\frac{1}{2}$	$\frac{1}{2}$
	B	-	6.52

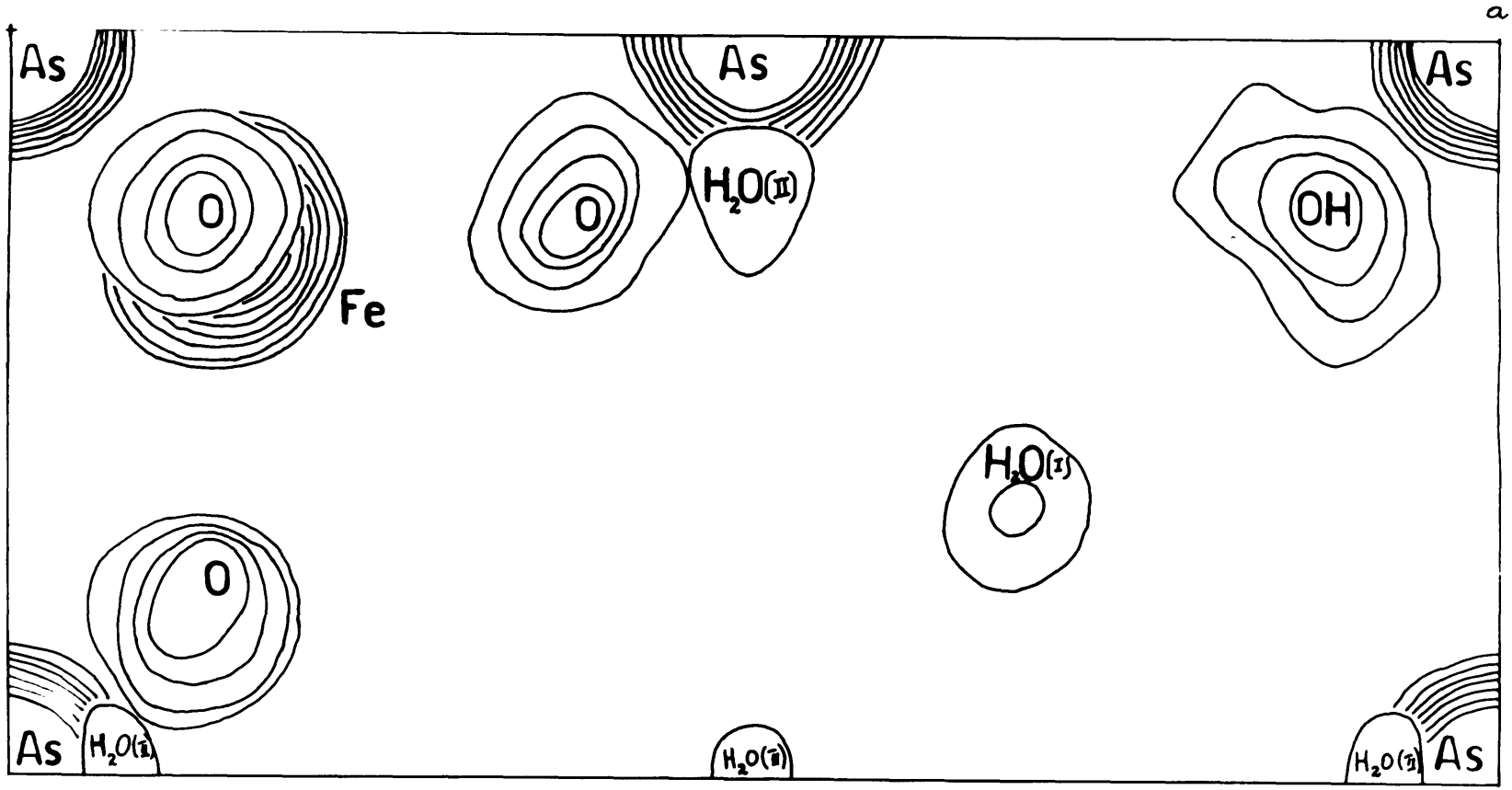

Fig. 2. Composite of the sections which contain maxima taken from the final electron-density function of the pharmacosiderite structure.

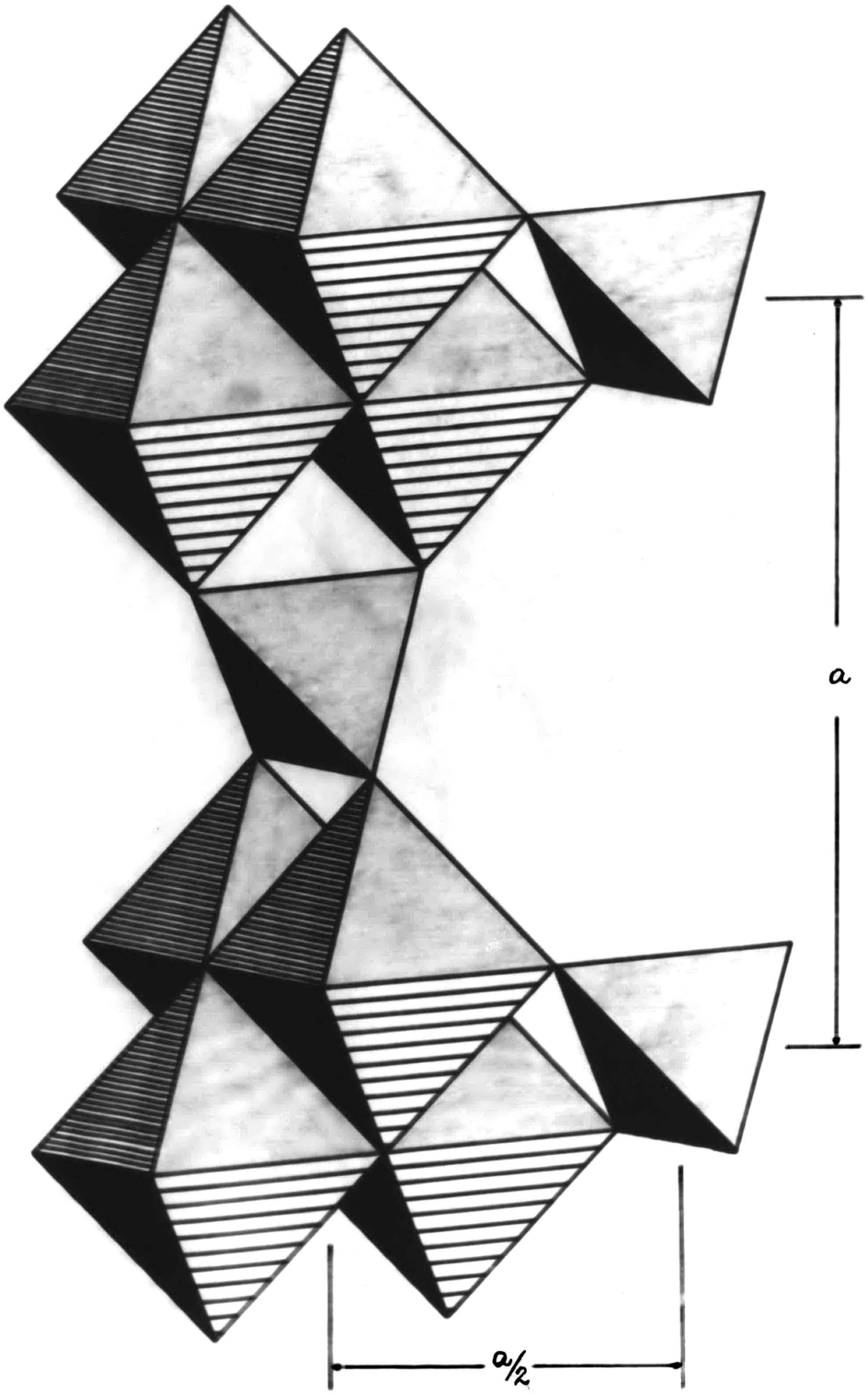

Fig.3. The linkage of the AsO_4 tetrahedra to the four $Fe(OH)_3O_3$ octahedra cluster in the pharmacosiderite structure.

atoms take the tetrahedrally coordinated site of the As atom in pharmacosiderite, and the other four Ge atoms take the octahedrally coordinated site of the Fe atom. In $Li_3HGe_7O_{16} \cdot 4H_2O$, the three Li atoms are distributed statistically, $\frac{3}{2}$ Li at 0 $\frac{1}{2}$ $\frac{1}{2}$ and $\frac{3}{2}$ Li at x $\frac{1}{2}$ $\frac{1}{2}$ with $x = \frac{1}{6}$, that is, they would take the place of some of pharmacosiderite's water molecules in the channels of the structure.

The final three-dimensional electron-density map $\rho(xyz)$ and the final difference-synthesis map $\Delta\rho(xyz)$ are given in the Appendix. The electron-density map shows no additional peaks that could be interpreted as extra atoms in the structure. The only important peak, which appears on section x = 0 with a height $\approx \frac{1}{3}$ of an oxygen atom, is too close to the Fe atom on section 4 to be a possible atom. However, there is an important anomaly observed on the electron-density map: the height of the water molecules H_2O (I) and H_2O (II) are not comparable to the average height of the oxygen atoms. In fact the height of H_2O (I) is $\frac{2}{5}$ the height of an oxygen atom, and the height of H_2O (II) is only $\frac{1}{6}$ of an oxygen peak. H_2O (II) was expected to have a height of about $\frac{1}{2}$ of an oxygen since three water molecules fill six equivalent positions. In order to interpret this low peak height as the water molecules being misplaced, negative peaks should be found in the corresponding locations of the difference synthesis map, which is not the case. The $\Delta\rho$ map is practically flat at the locations assigned to H_2O (I) and H_2O(II). On the other hand, the temperature factor of both water molecules are too high, as shown in Table 7, and with such temperature coefficients the peak height in the $\rho(xyz)$ map is expected to be much lower than the normal[25]. This is confirmed by the fact that, at an R factor of 16.6 %, before starting the refinement of the temperature coefficients, the height of H_2O (I) on an electron-density map was equal to a normal oxygen height, and the height of H_2O (II) was the expected $\frac{1}{2}$ of an oxygen. All these facts point out that what should have been adjusted was not the temperature coefficients but the multiplicity of the water molecules at the positions indicated. Since the adjustment of the para-

meters was left to the least-squares refinement program, and the multiplicity was not allowed to change, the program changed the parameter whose role was closest to the multiplicity factor, that is, the temperature coefficients. It is possible then, that further refinement of the structure, taking these facts into account, would indicate a statistical distribution of the water molecules, giving a smaller number of molecules to the positions assigned to waters I and II.

The remaining water molecules would possibly go to a position such as 0 $\frac{1}{2}$ $\frac{1}{2}$. Even if this position does not show a peak on the electron-density map, it shows a maximum on the $\Delta\rho$ map. The height of the maximum on the $\Delta\rho$ map is about half the height of the peak representing the H_2O(II) water molecule on the ρ map.

The principal interatomic distances of the structure as computed from the final atomic coordinates are listed in Table 8. Distances corresponding to the AsO_4 tetrahedra and to the $Fe(OH)_3O_3$ octahedra are in good agreement with previous publications[26, 27, 28, 29, 30].

Table 8

Principal interatomic distances in the pharmacosiderite structure

		Distance	Multiplicity of the distance
AsO_4 tetrahedron	As - O	1.66 Å	4
	O - O	2.80	2
	O - O	2.68	4
$Fe(OH)_3O_3$ octahedron	Fe - O	2.06	3
	Fe - OH	2.04	3
	OH - OH	2.48	3
	O - OH	2.89	6
	O - OH	3.97	3
	O - O	2.97	3
Minimum cation-cation distances	As - Fe	3.28	4
	Fe - Fe	3.21	6

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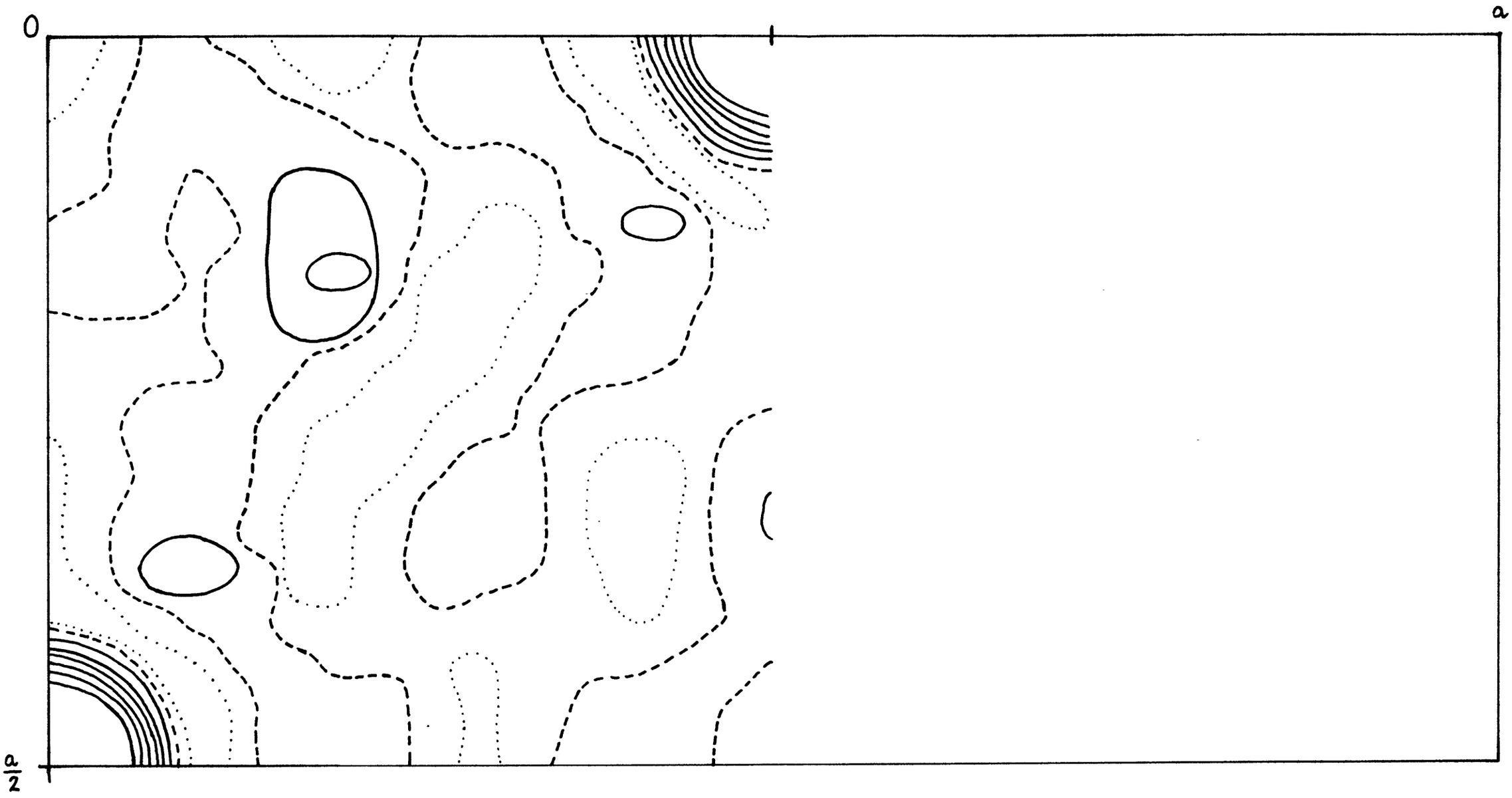
Appendix

Sixteen sections of the electron-density map $\rho(xyz)$ and the sexteen sections of the difference synthesis map $\Delta\rho(xyz)$ corresponding to an R of 12.3 % are shown. For the computations, the cell's edge was divided into 30 parts, so the set of maps represents one quarter of the unit cell.

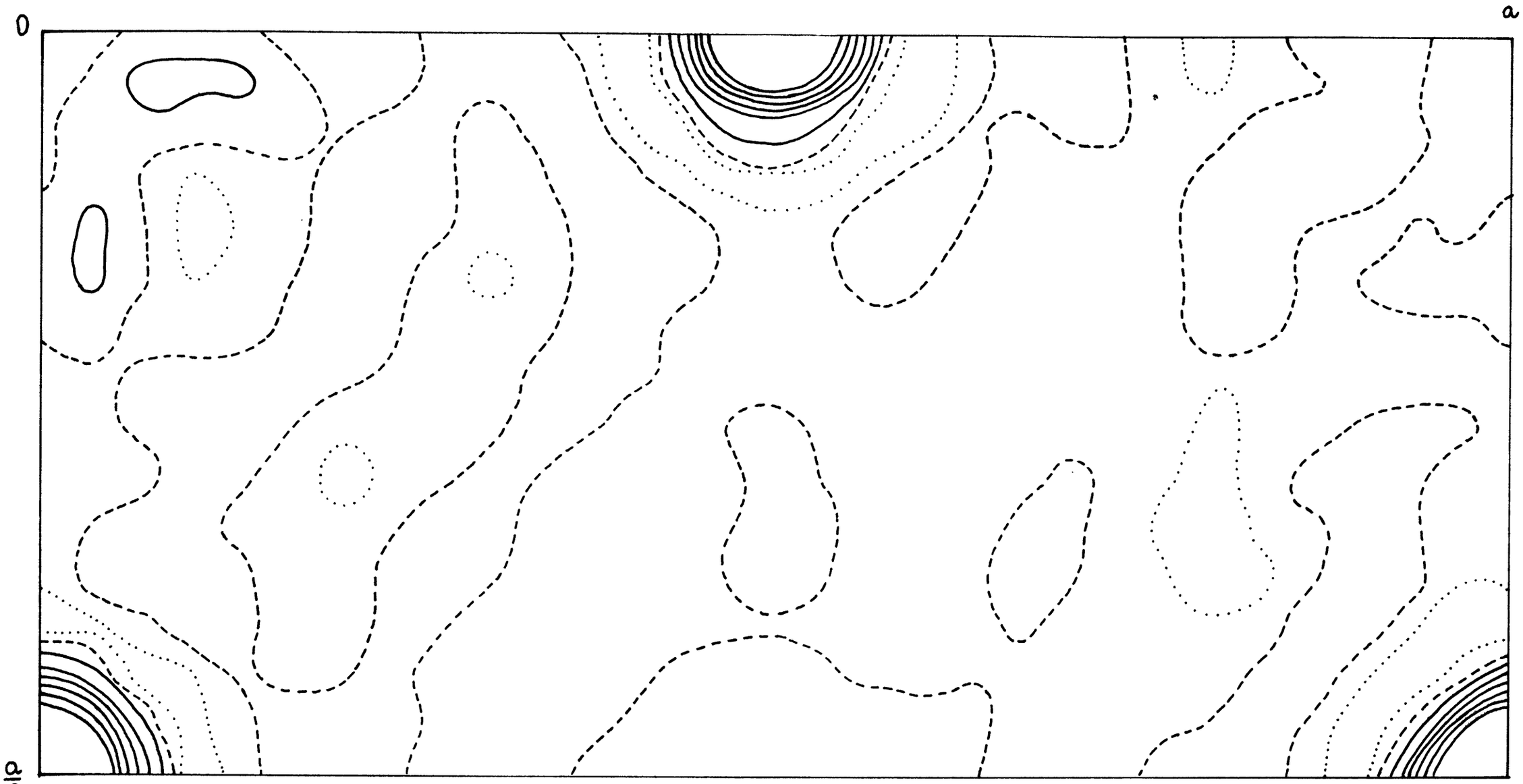
In both sets of sections the positive contours have been drawn with full line, the zero contour with a dashed line and the dotted line represents the negative contours. The contours have been drawn at arbitrary but equal intervals. Only a few contours of the Fe and As atoms have been represented, but the actual relation of the average Fe peak height to the average 0 peak height is approximately 1300/300 and this relation is 1700/300 for an As peak compared to an 0 peak. Each contour on the $\rho(xyz)$ map corresponds to five contours on the $\Delta\rho(xyz)$ map.

The axes were chosen as follows: x axis, normal to the sheet; y axis, parallel to the vertical direction; and z axis, parallel to the horizontal direction. The atomic positions are indicated by a cross on the section closest to the corresponding x coordinate. In particular, the sections containing the atoms are: $x = 0$, As atom; $x = 3/30$, an OH radical and the oxygen from the H_2O (II) molecule; $x = 4/30$, Fe atom and two oxygen atoms; $x = 9/30$, the oxygen from the H_2O (I) water molecule; and $x = 12/30$, the third oxygen atom of the asymmetric unit. Only half of the specific sections (0yz) and $(\frac{1}{2}yz)$ for ρ and $\Delta\rho$ are shown, since these sections present a mirror symmetry plane at $00\frac{1}{2}$ parallel to the y axis.

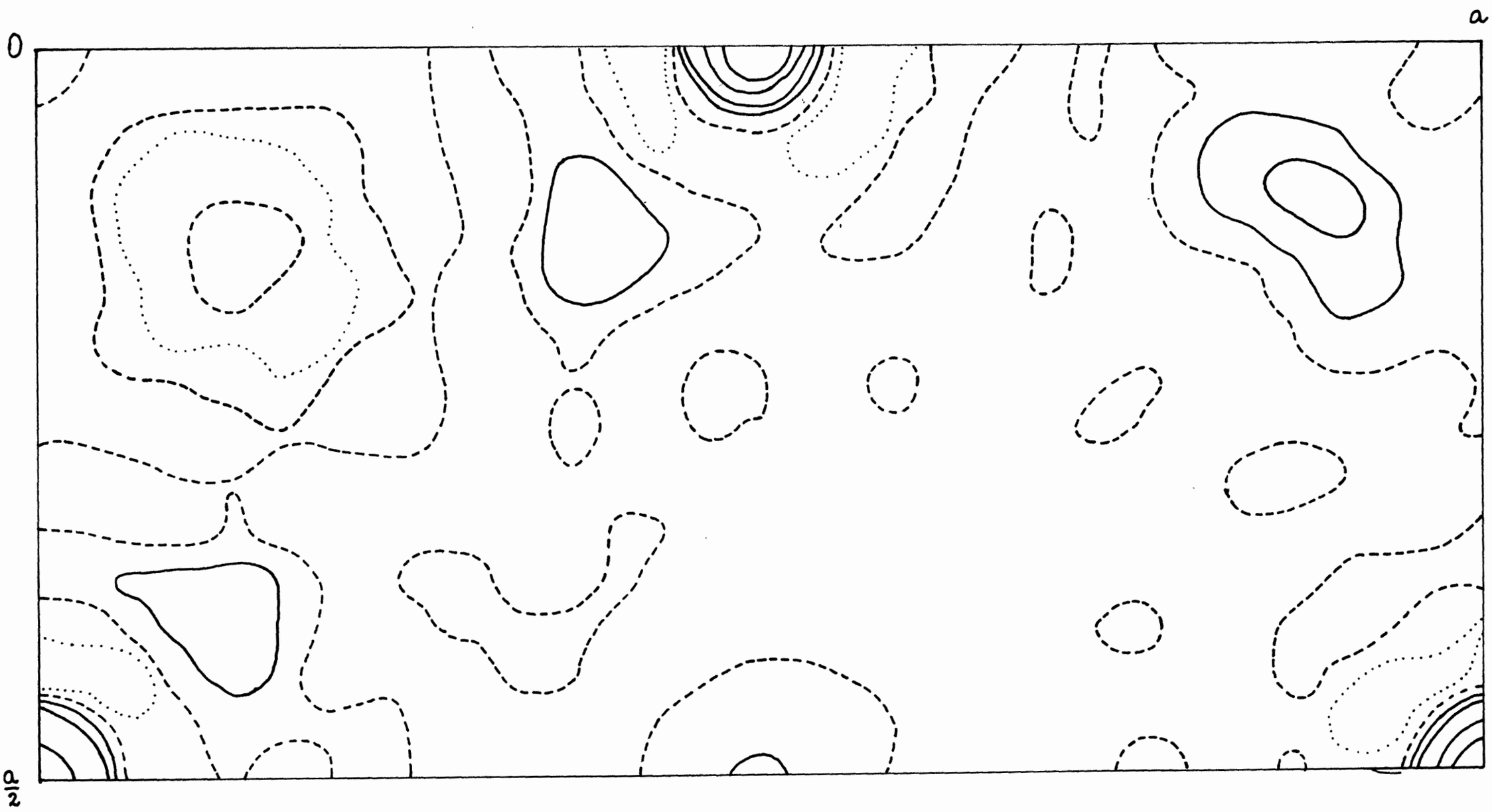
$\rho(0yz)$



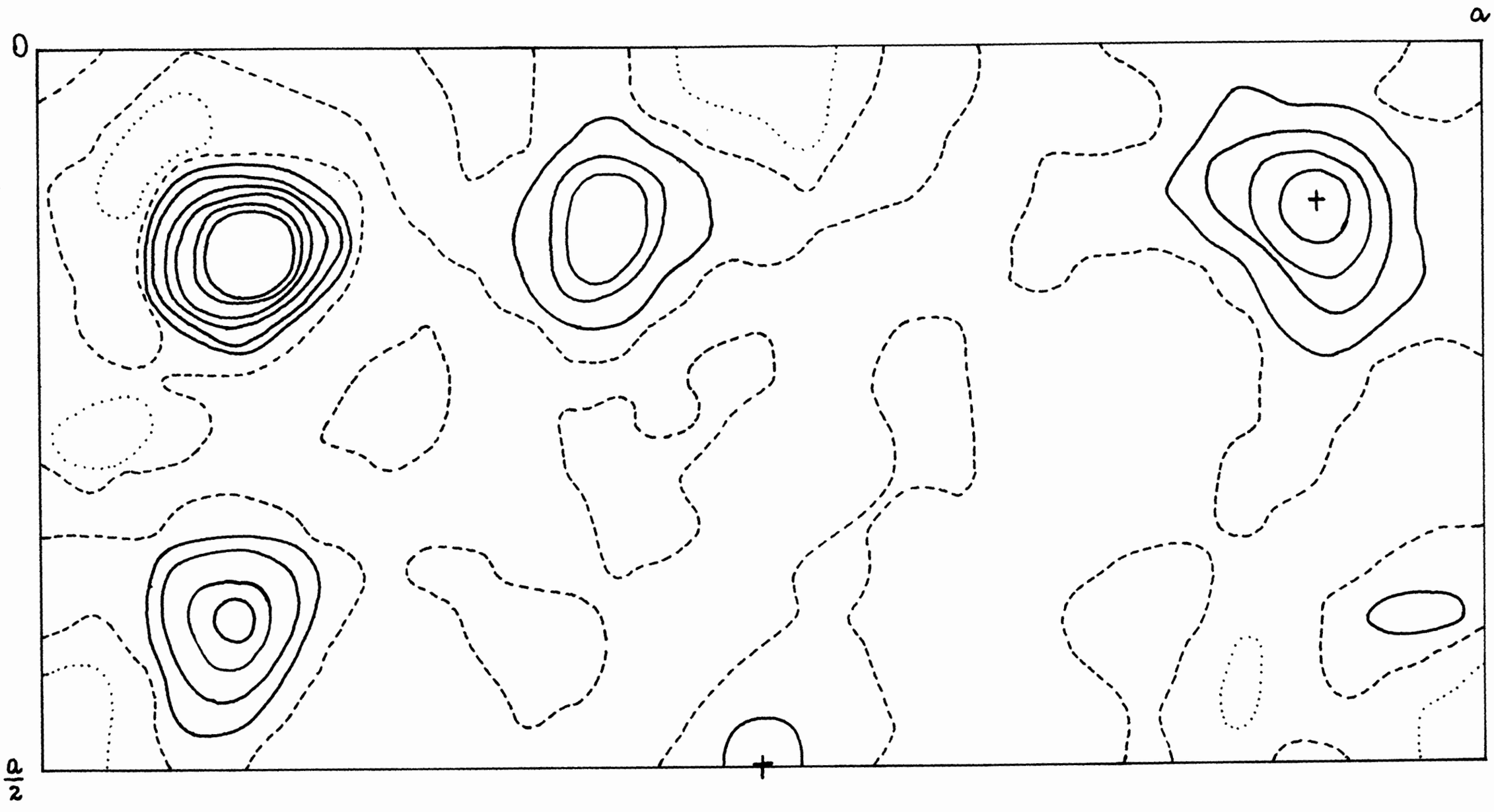
$\rho(\frac{1}{30}\, y\, z)$



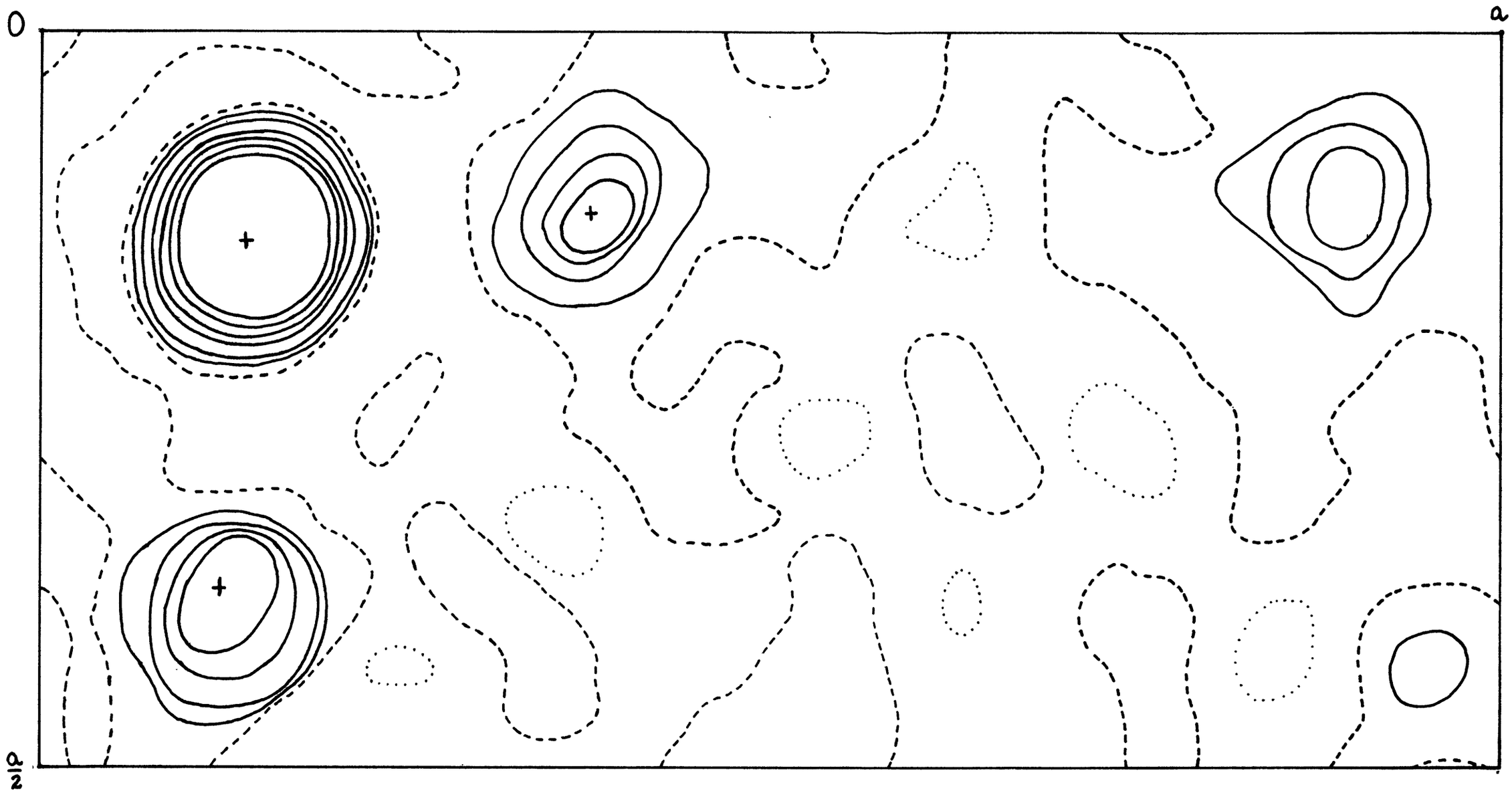
$\rho(\frac{2}{30}yz)$



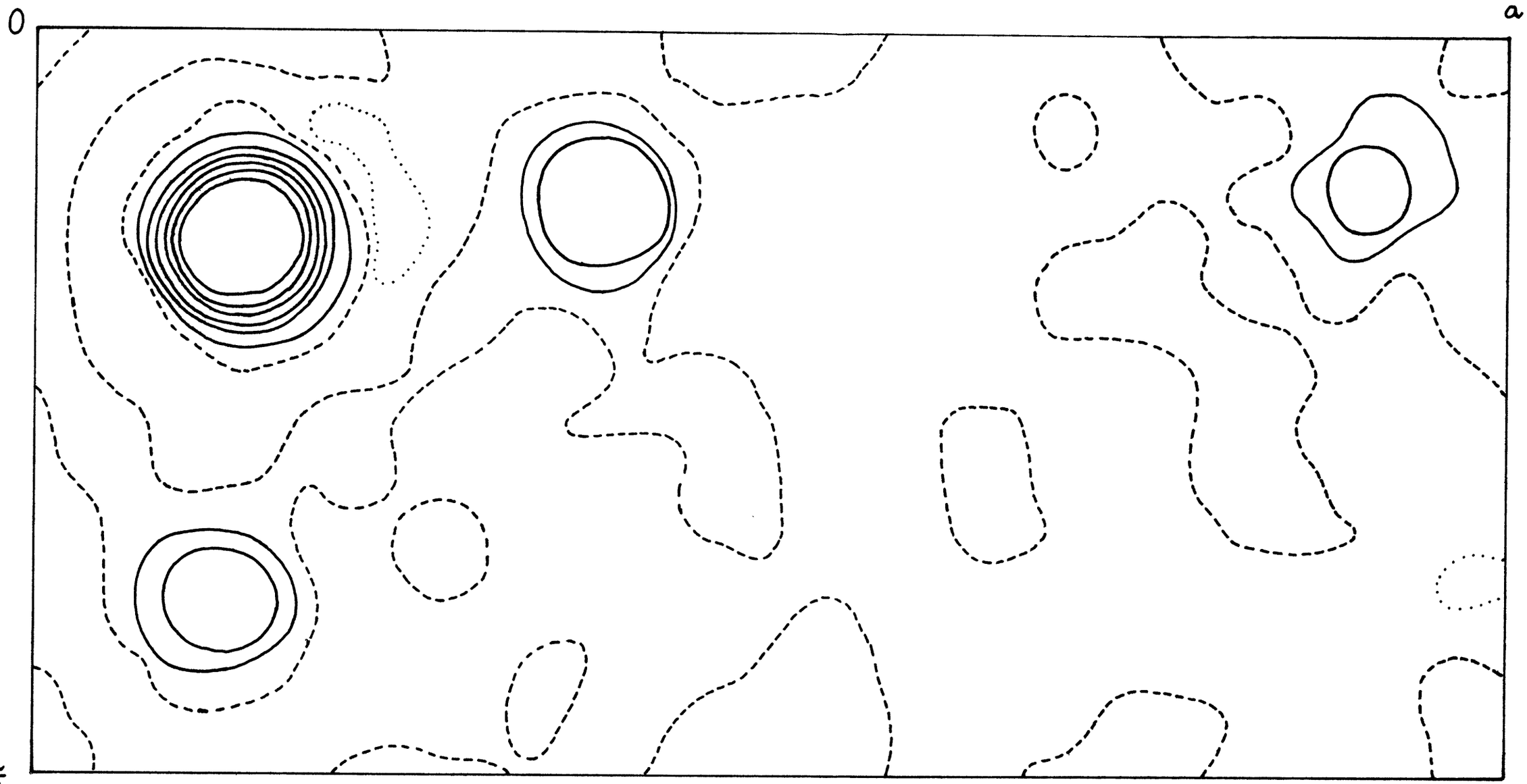
$\rho\left(\frac{3}{30}\, y\, z\right)$



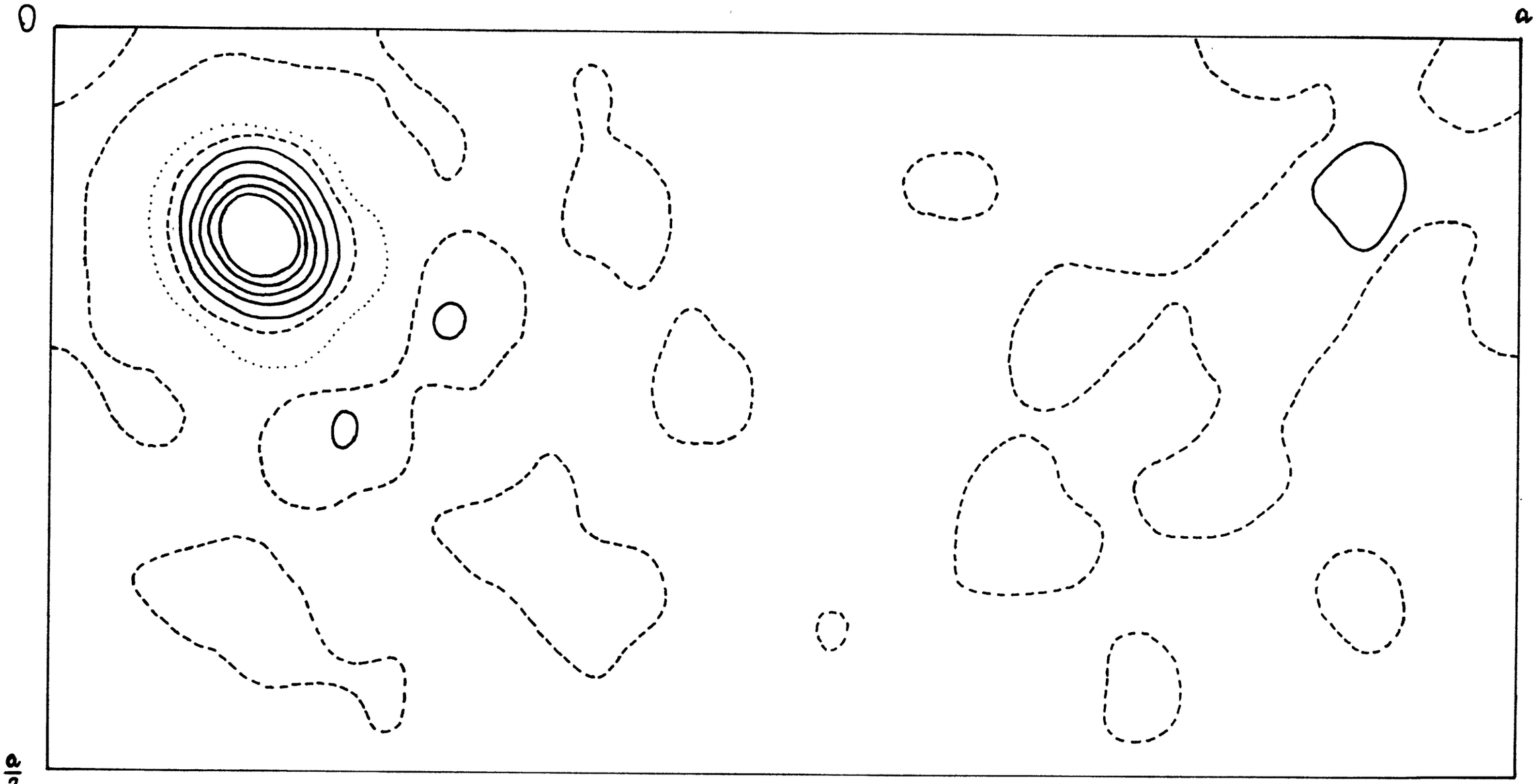
$\rho(\frac{4}{30}yz)$



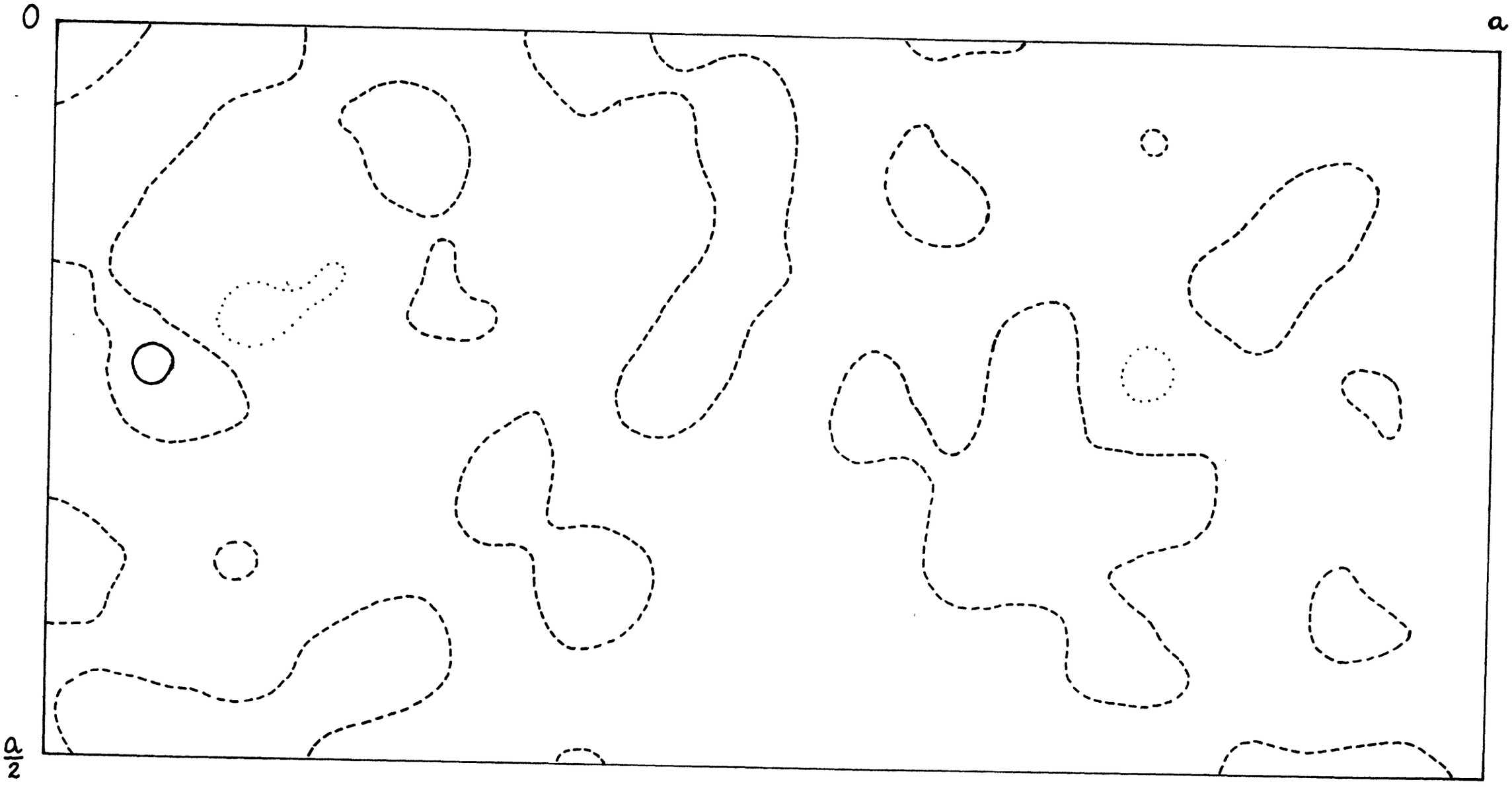
$\rho(\frac{5}{30}\ y\ z)$



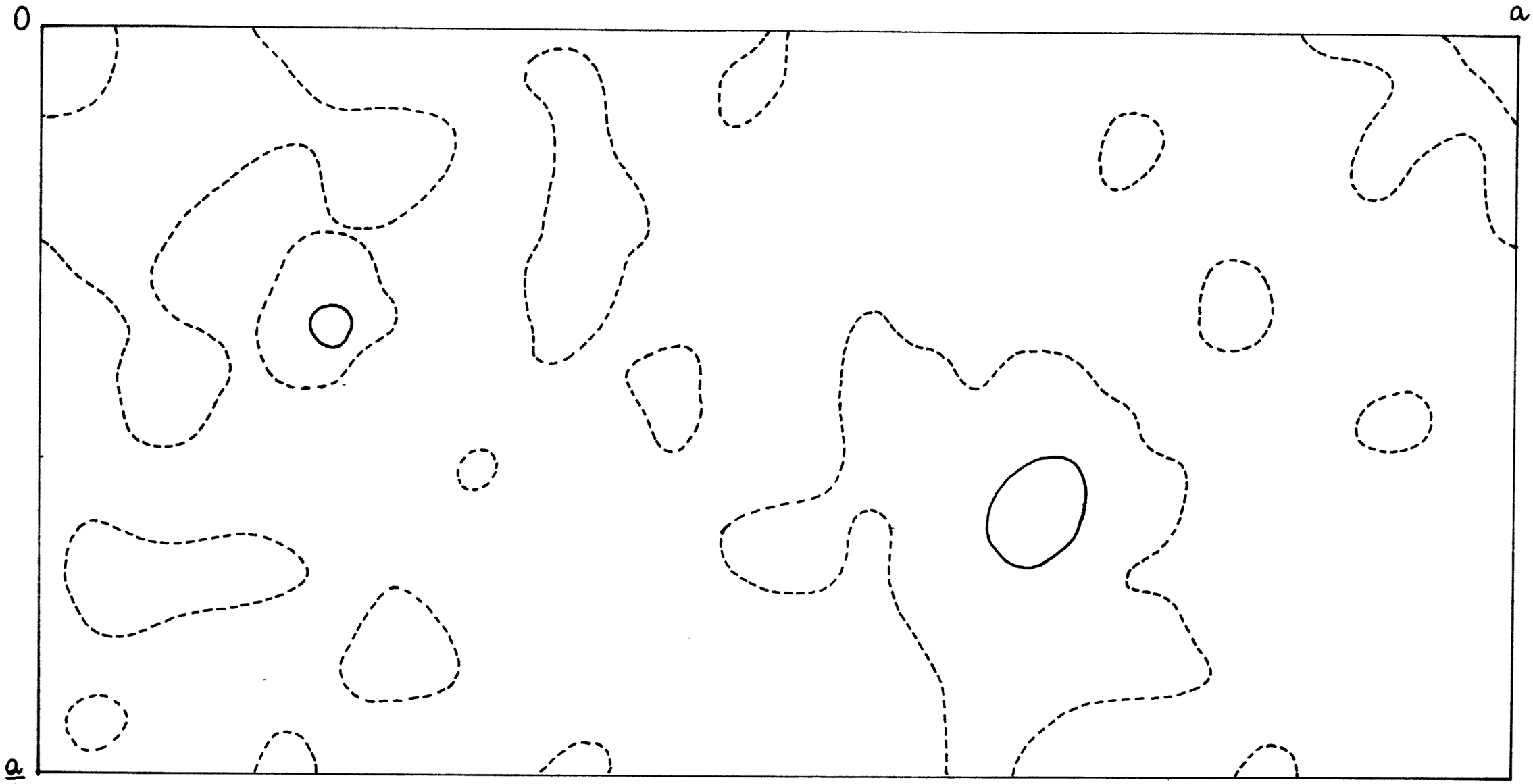
$\rho(\frac{b}{30}\, y\, z)$



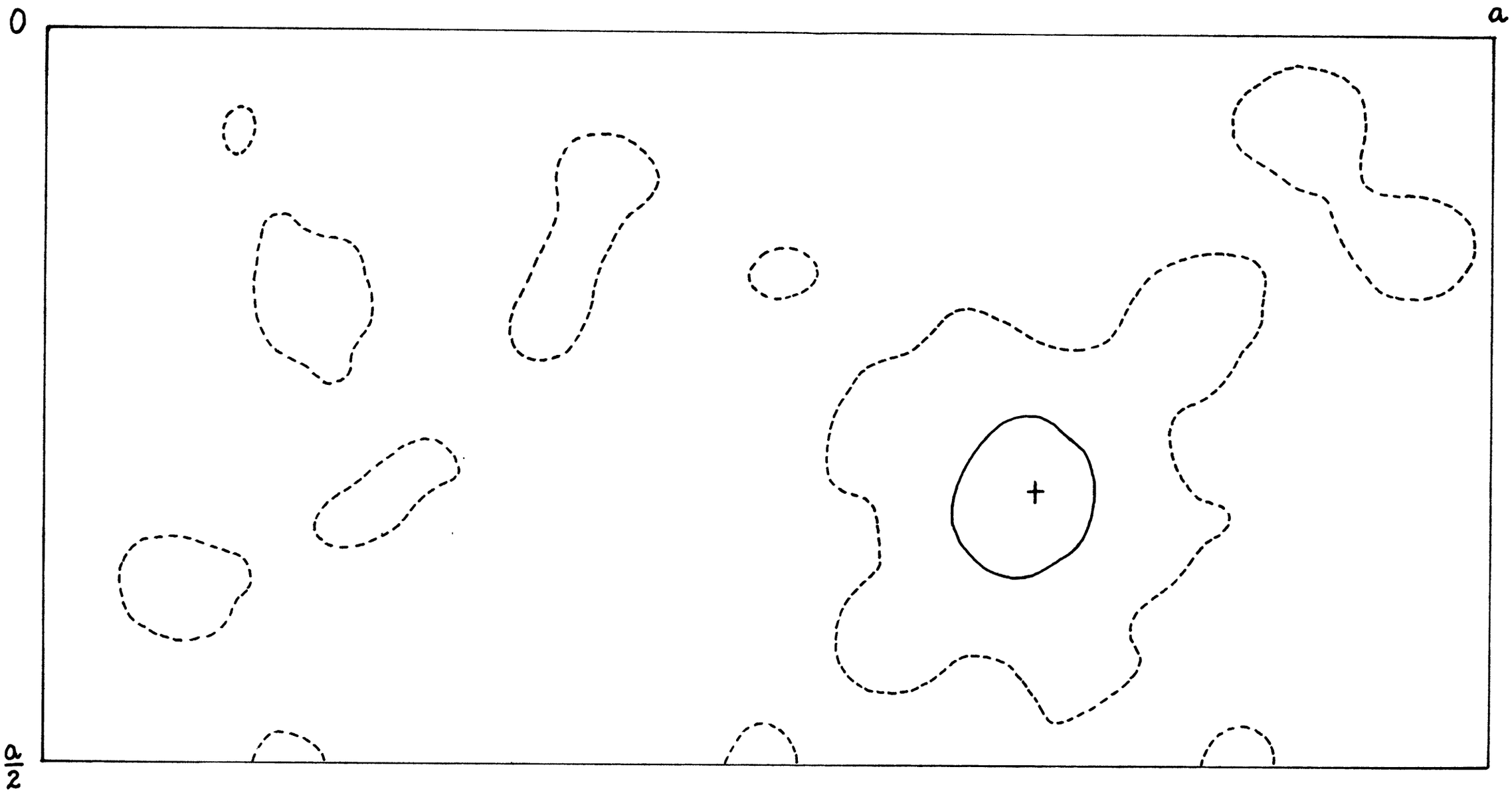
$\rho(\frac{7}{30}\ y\ z)$



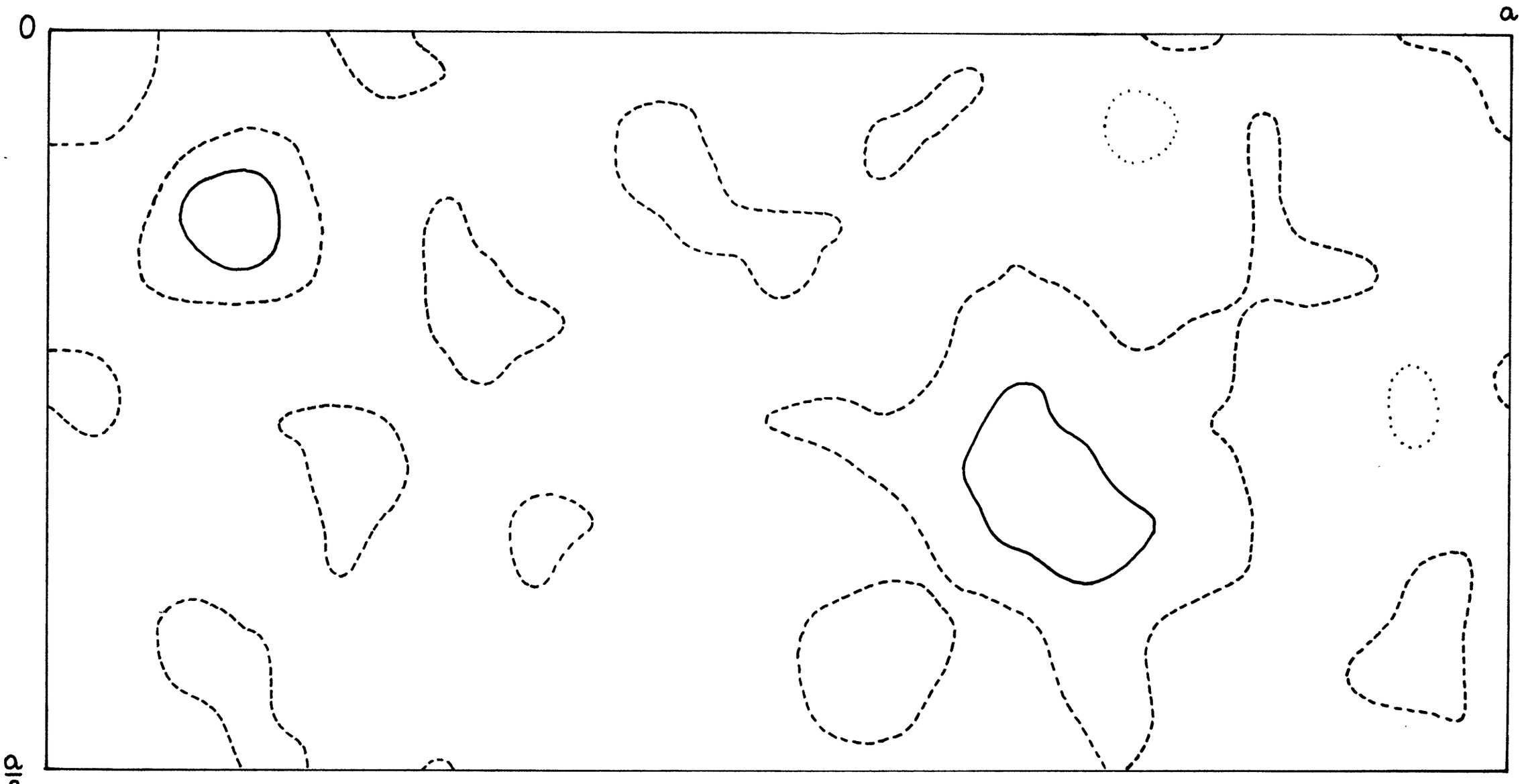
$\rho(\frac{8}{30}\,y\,z)$



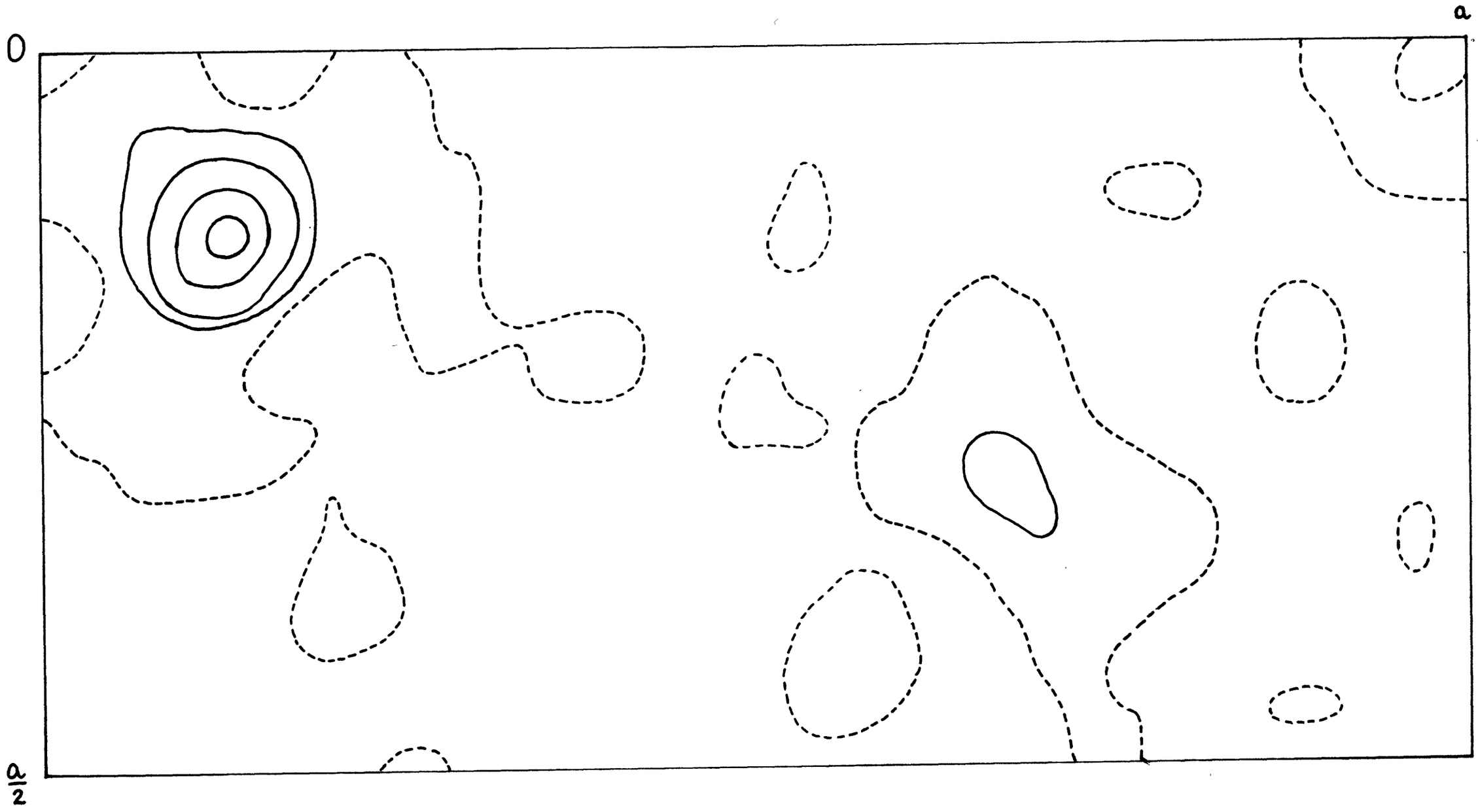
$\rho(\frac{9}{30}\, y\, z)$



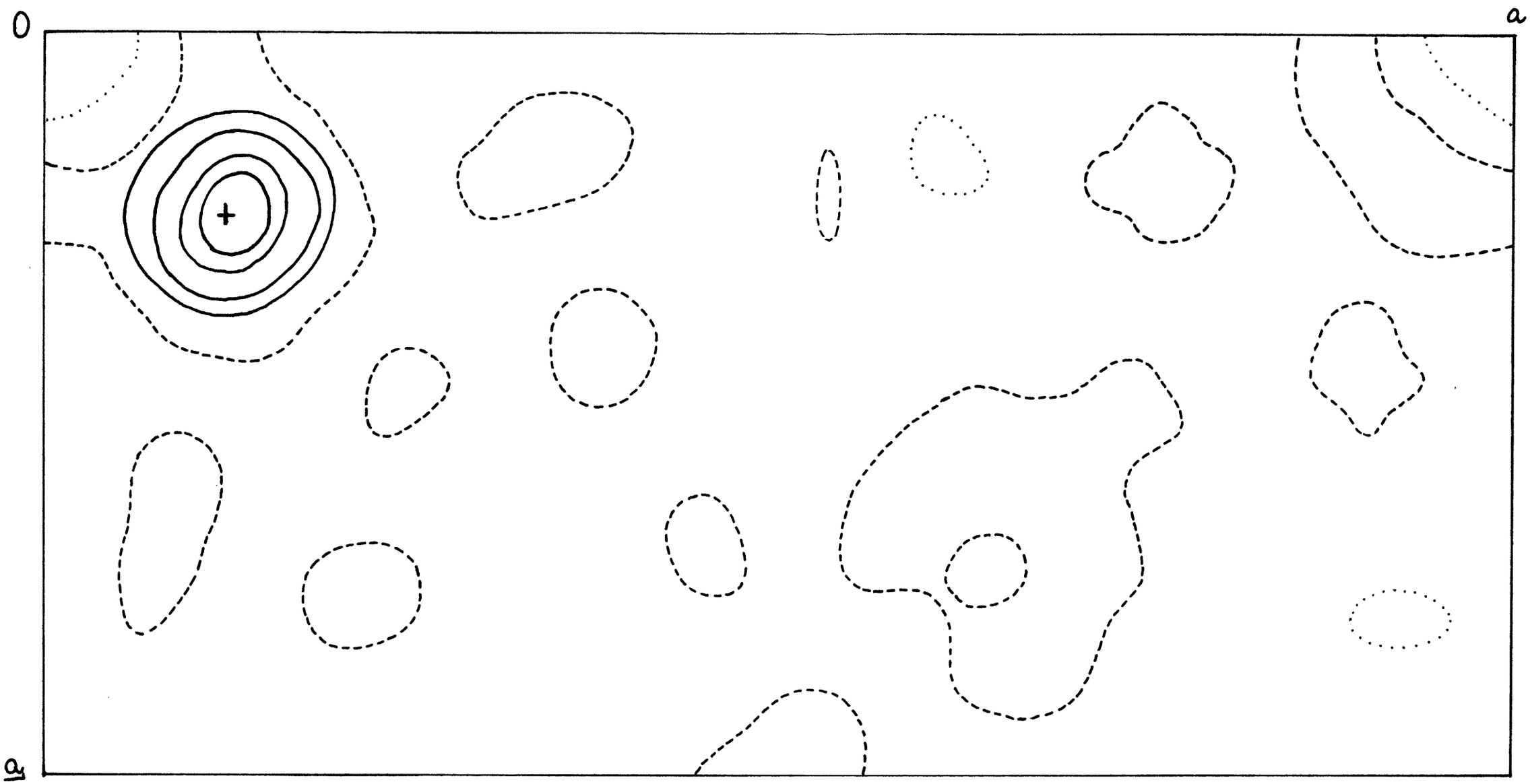
$\rho(\frac{10}{30}\ y\ z)$



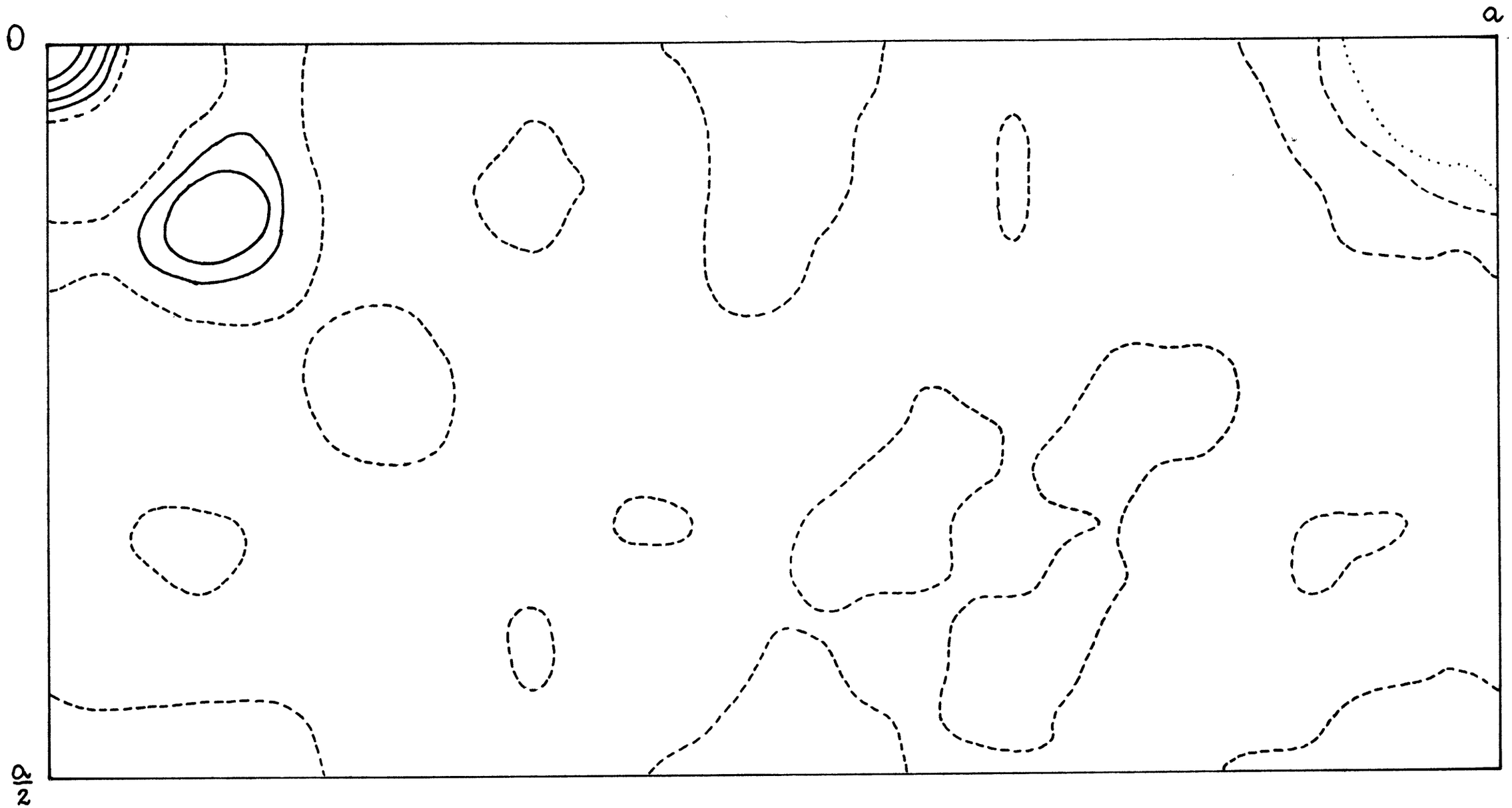
$\rho\left(\frac{11}{30}\, y\, z\right)$



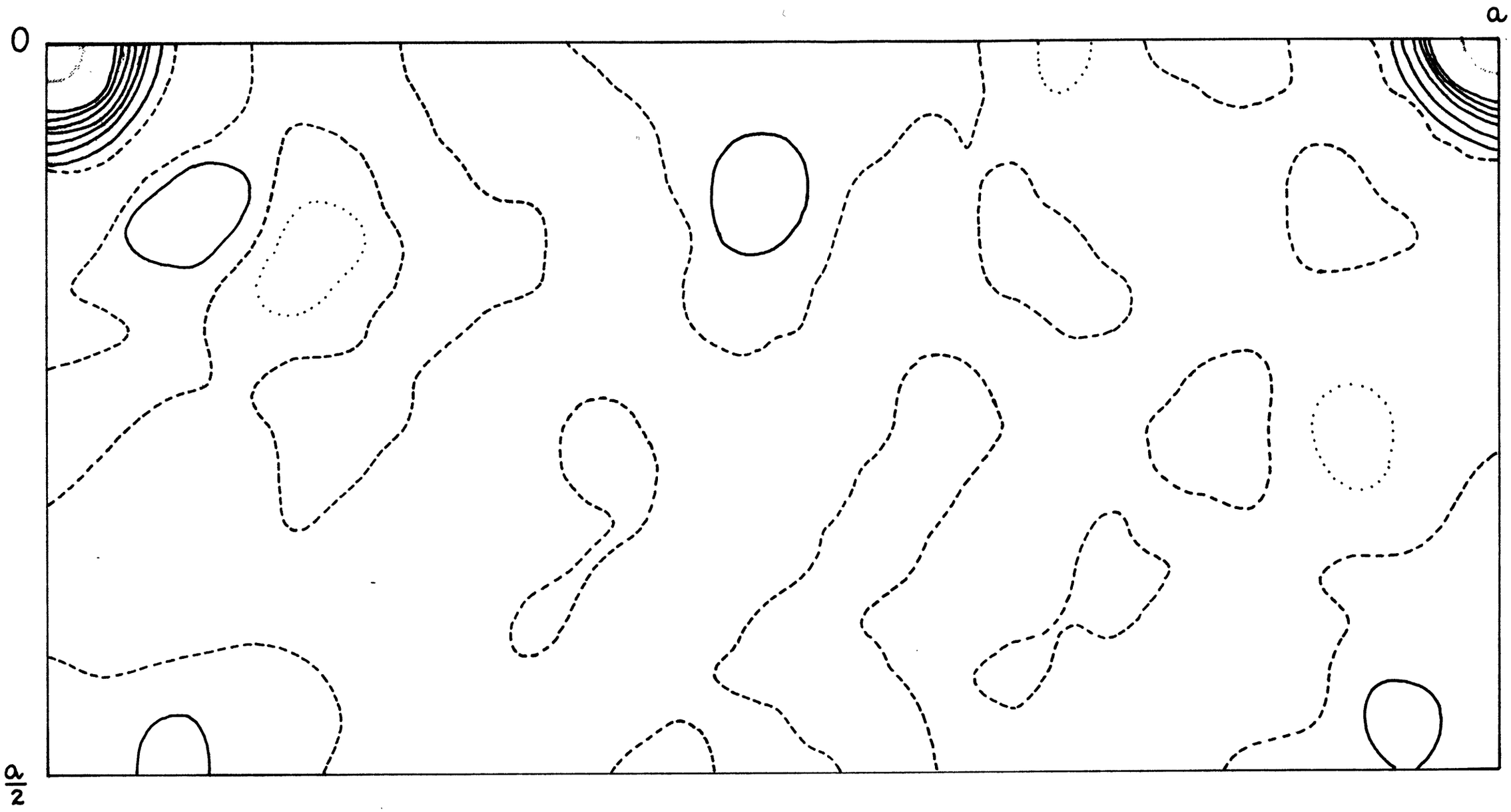
$\rho\left(\frac{12}{30}\, y\, z\right)$



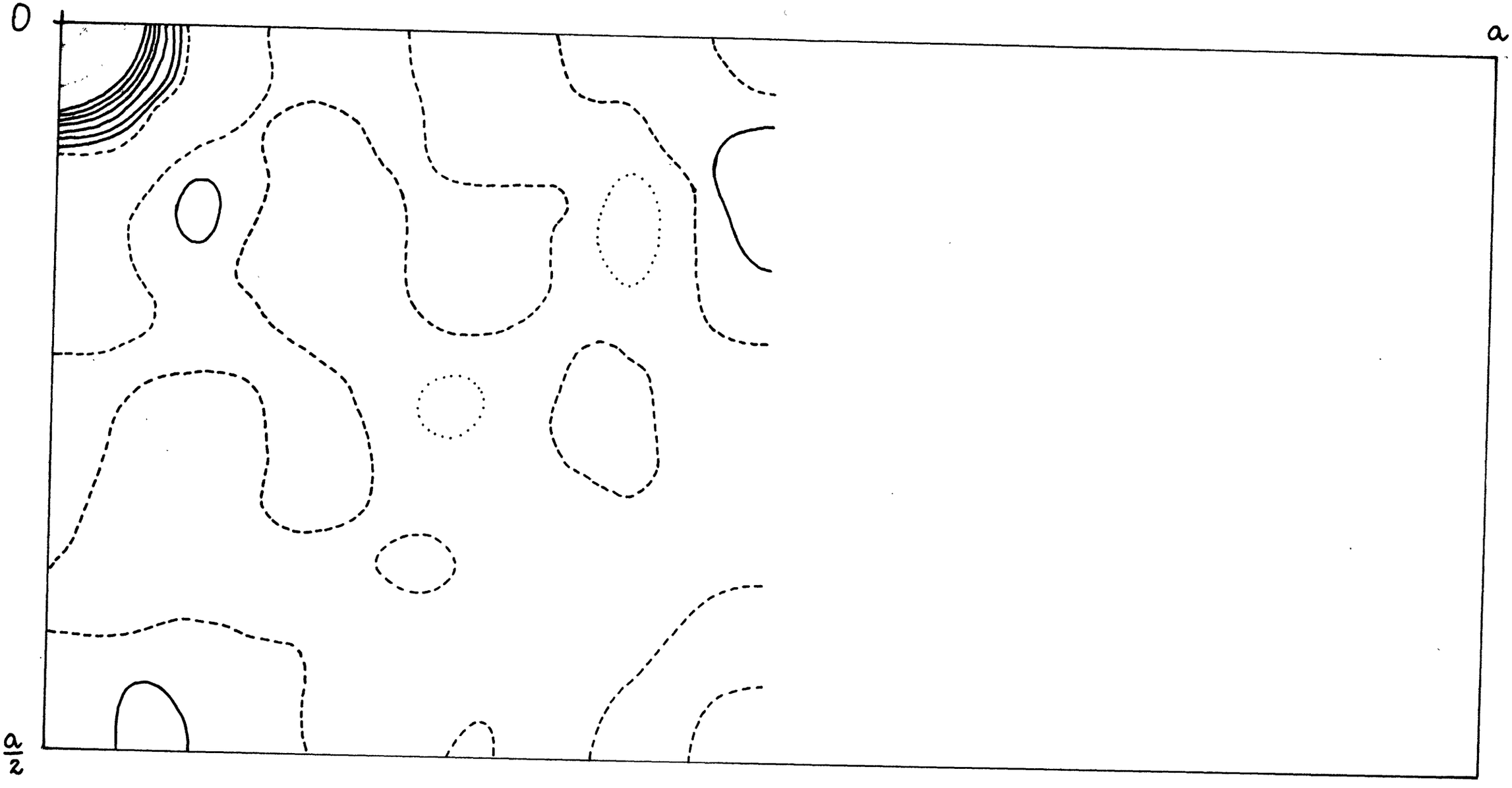
$\rho(\frac{13}{30}yz)$



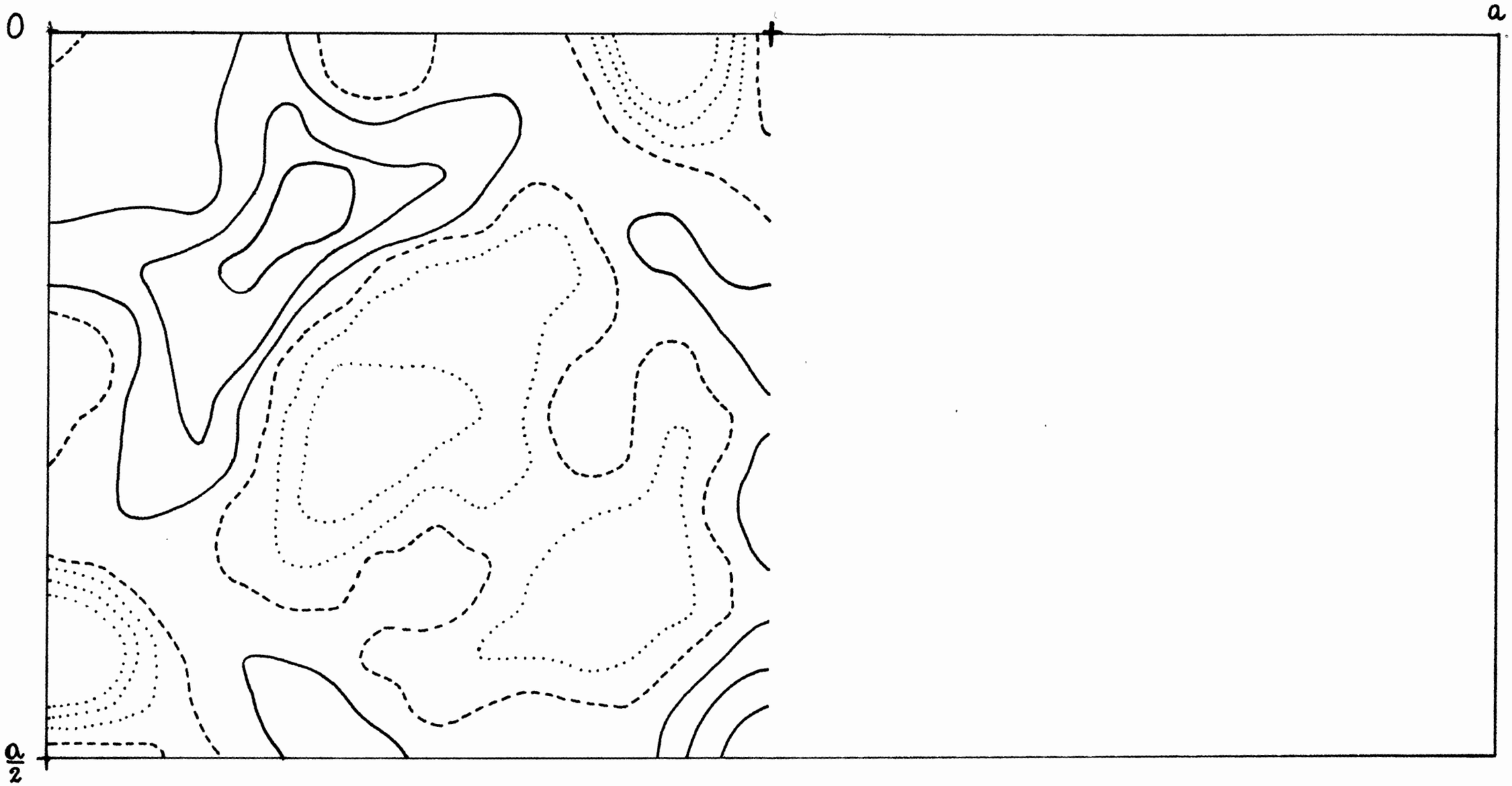
$\rho(\frac{14}{30}\, y\, z)$



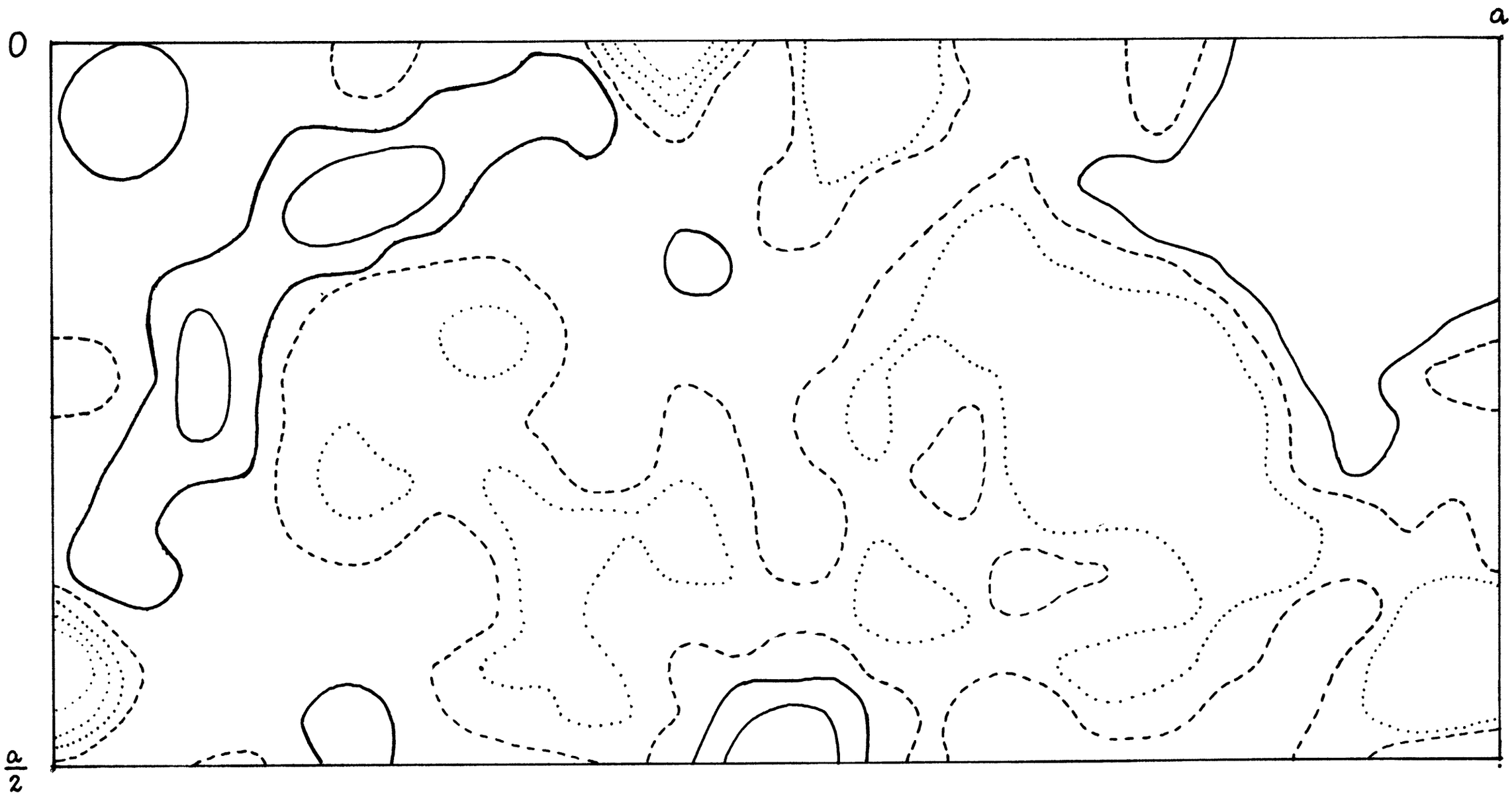
$\rho(\frac{1}{2}\,y\,z)$



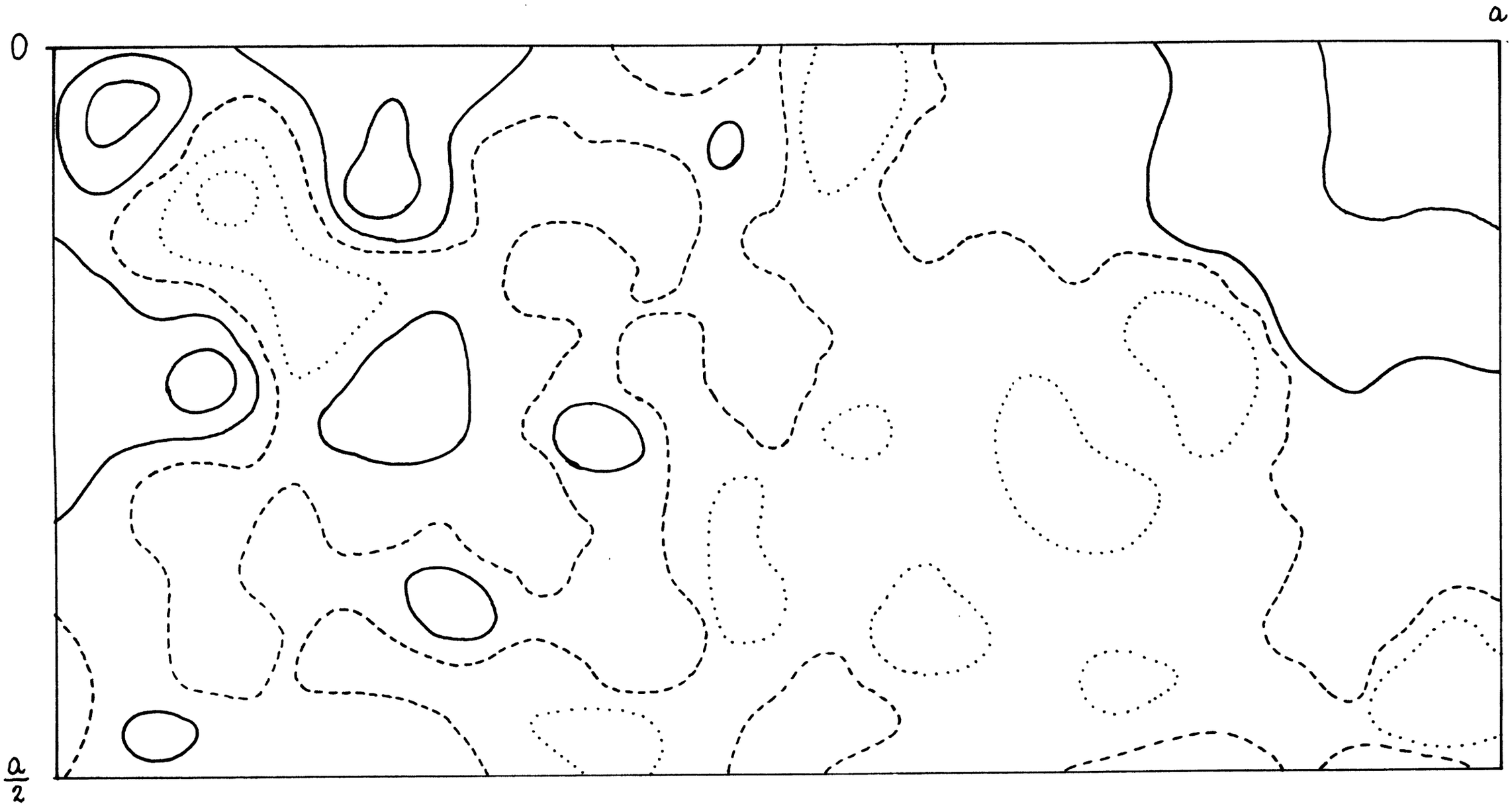
$\Delta\rho(0yz)$



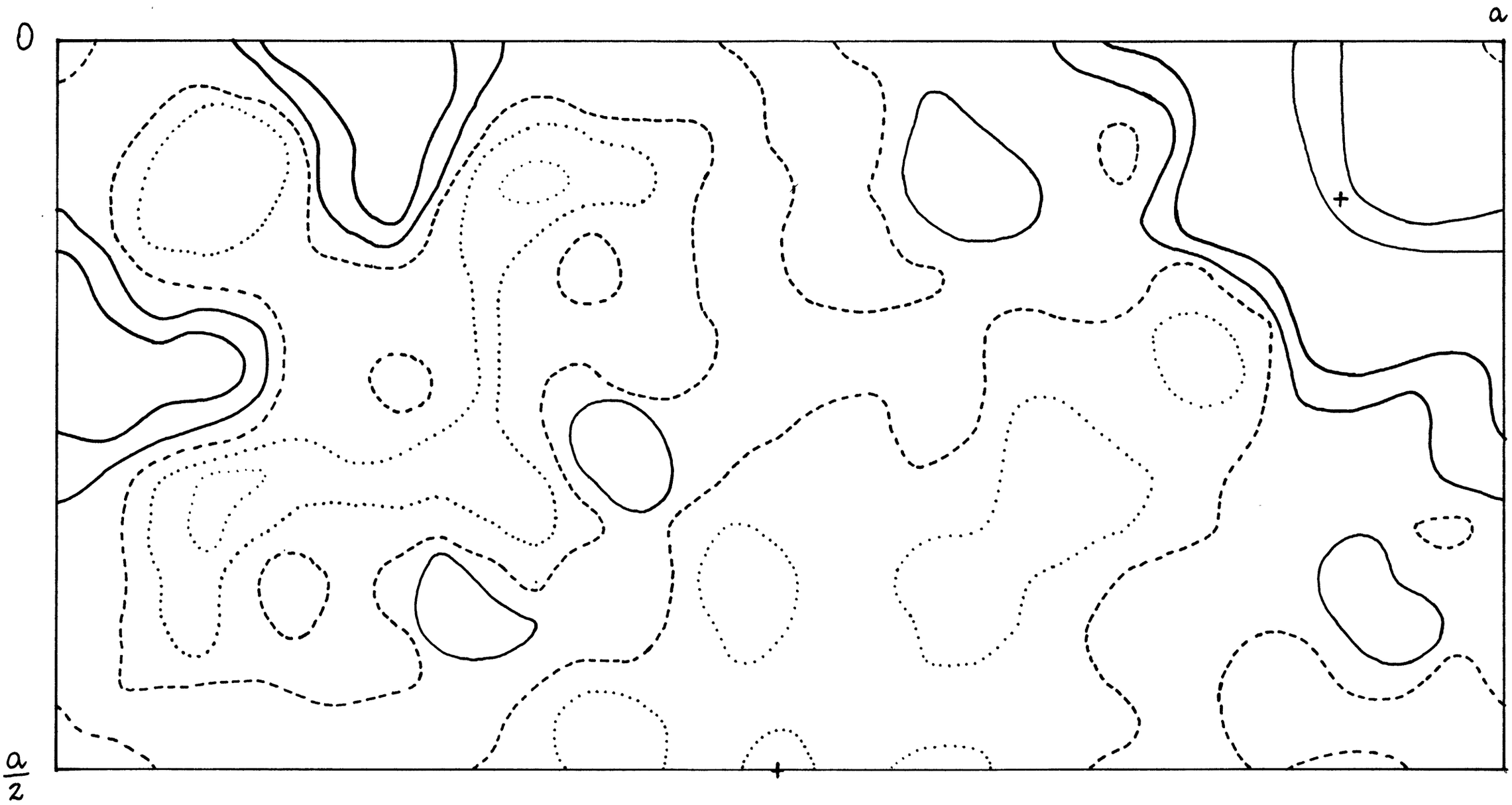
$\Delta\rho(\frac{1}{30}yz)$



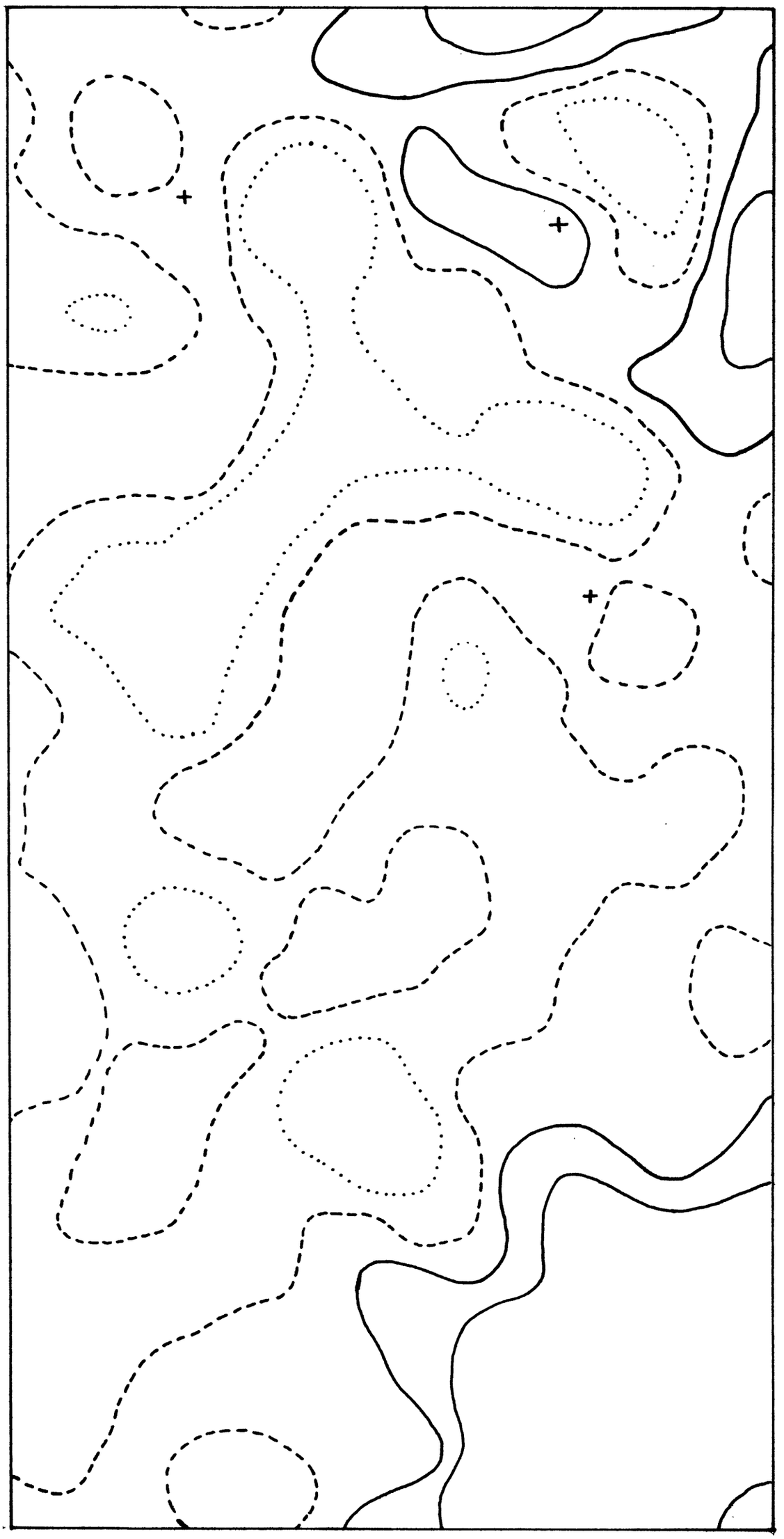
$\Delta\rho\left(\frac{2}{30}\, y\, z\right)$



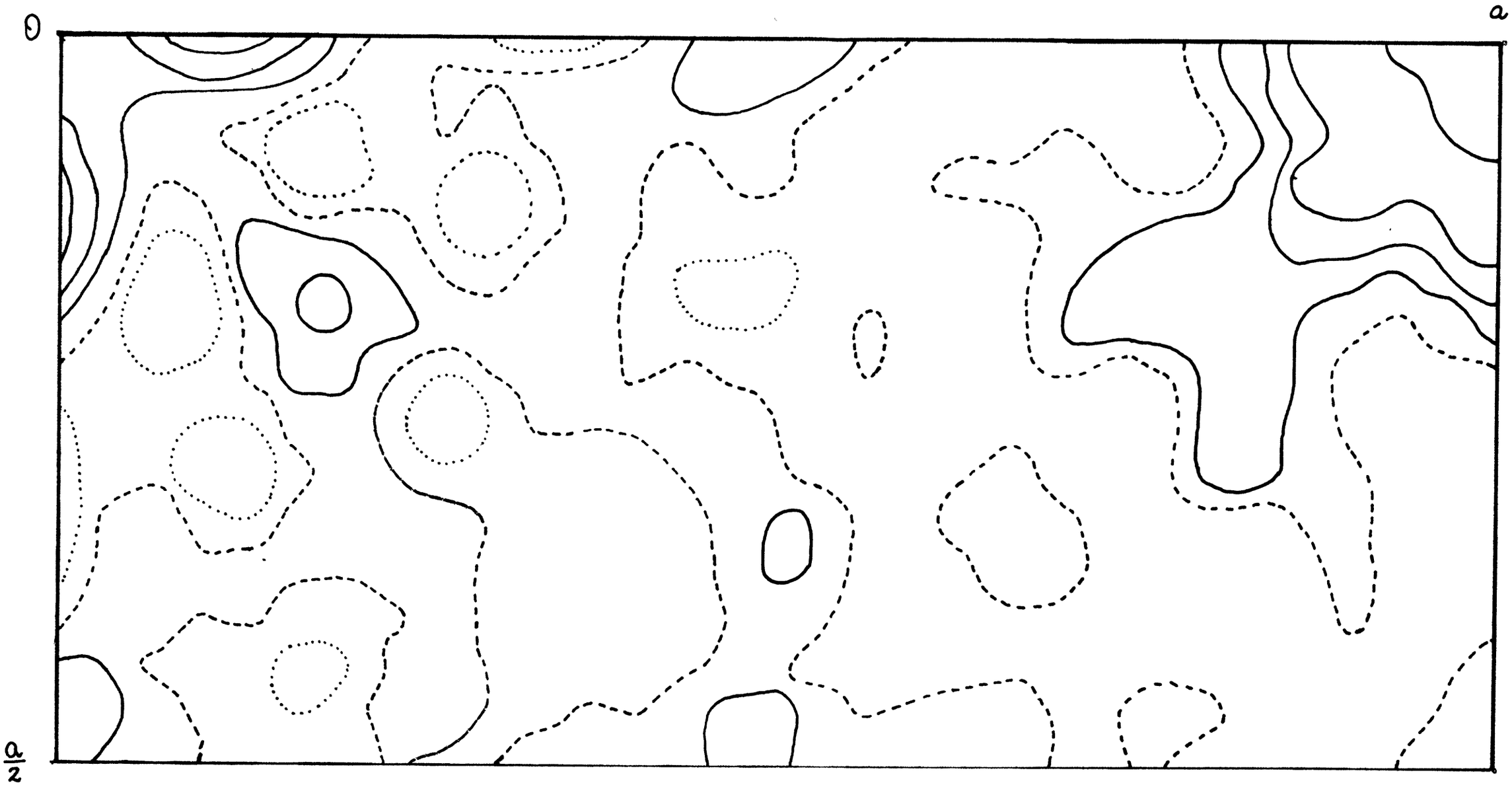
$\Delta\rho(\frac{3}{30}\,y\,z)$



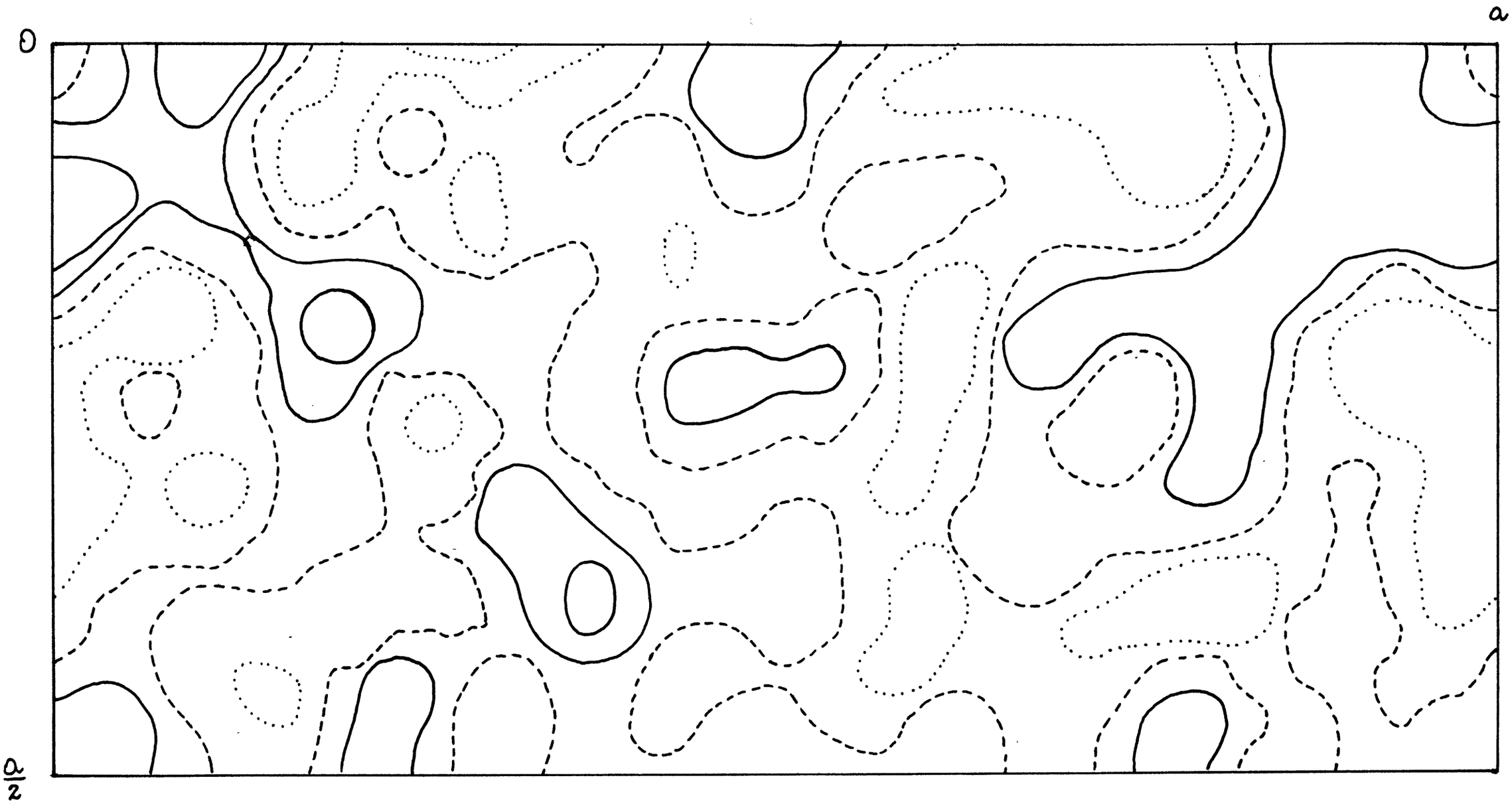
$\Delta\rho(\frac{4}{30}\ y\ z)$



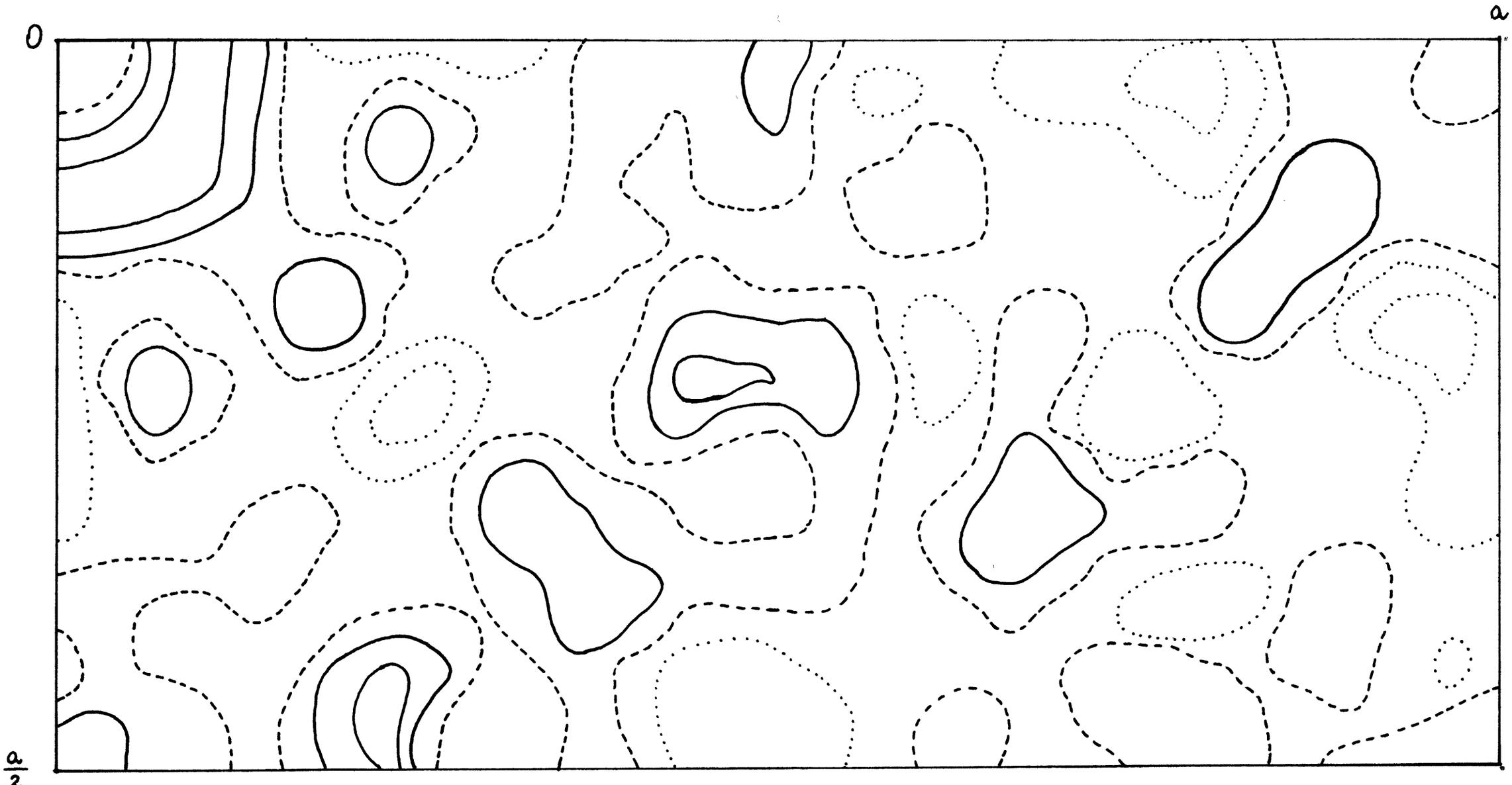
$\Delta\rho\left(\frac{5}{30}\,y\,z\right)$



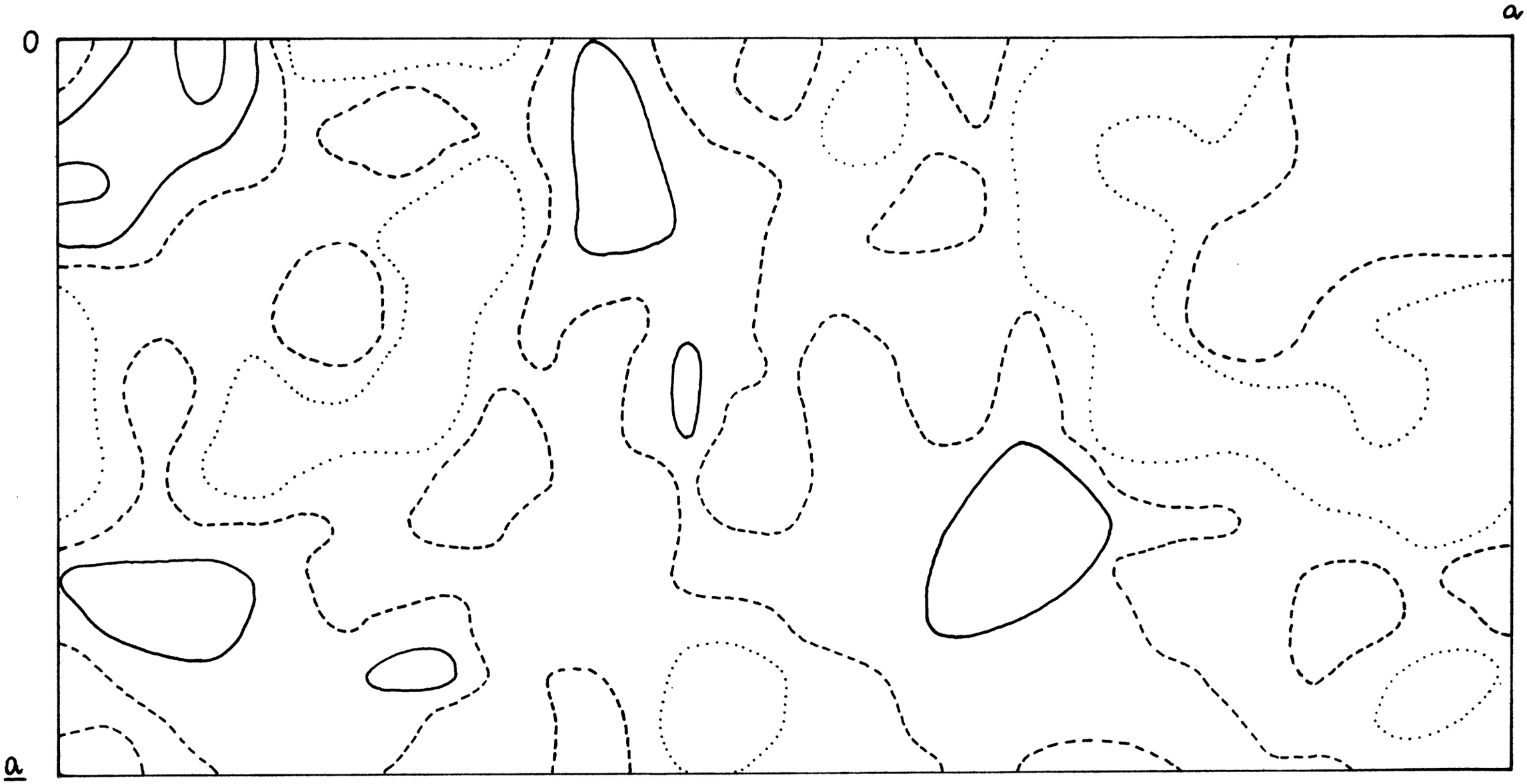
$\Delta\rho(\frac{6}{30}\, y\, z)$



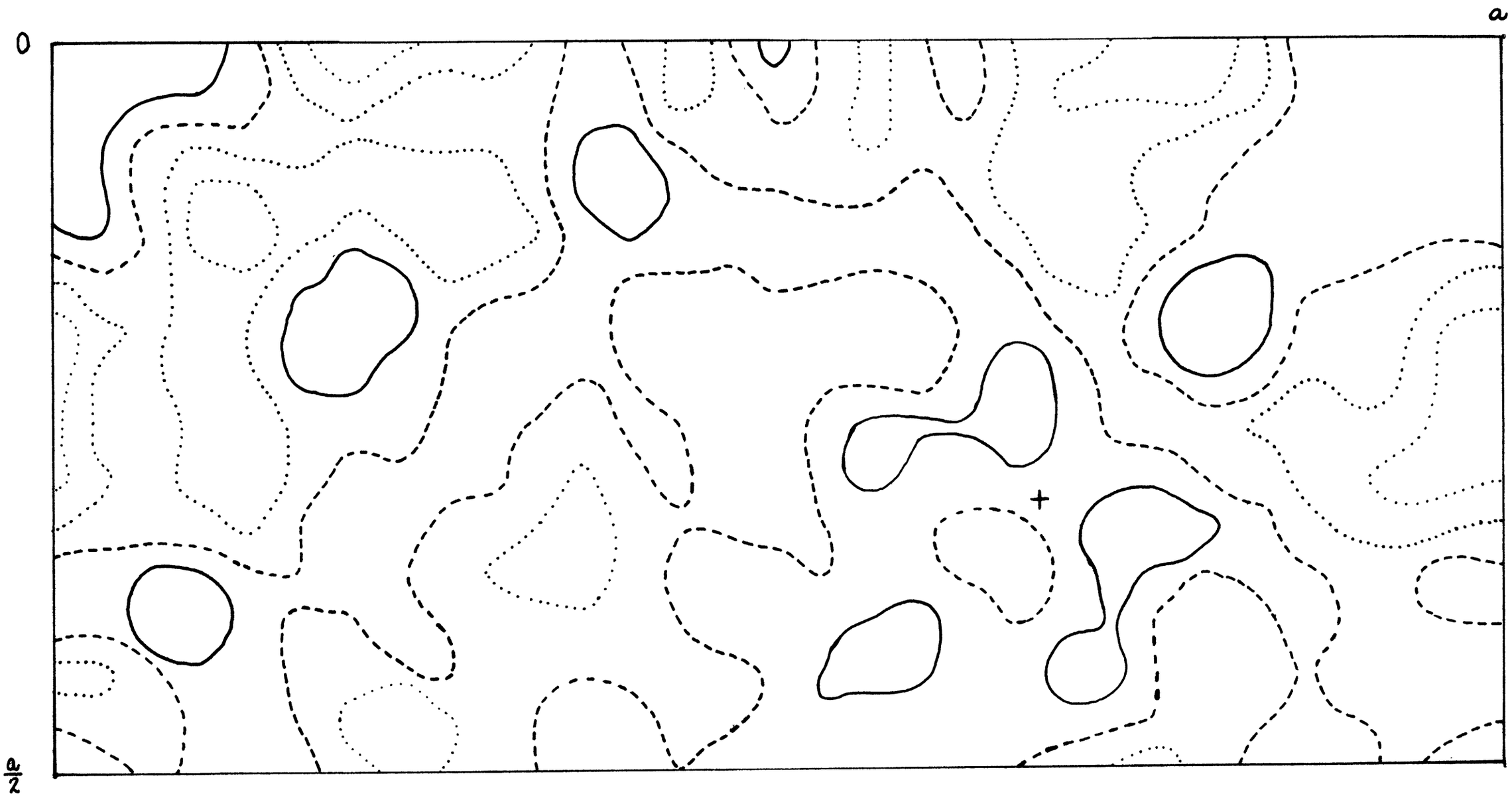
$\Delta\rho(\frac{z}{30}\,y\,z)$



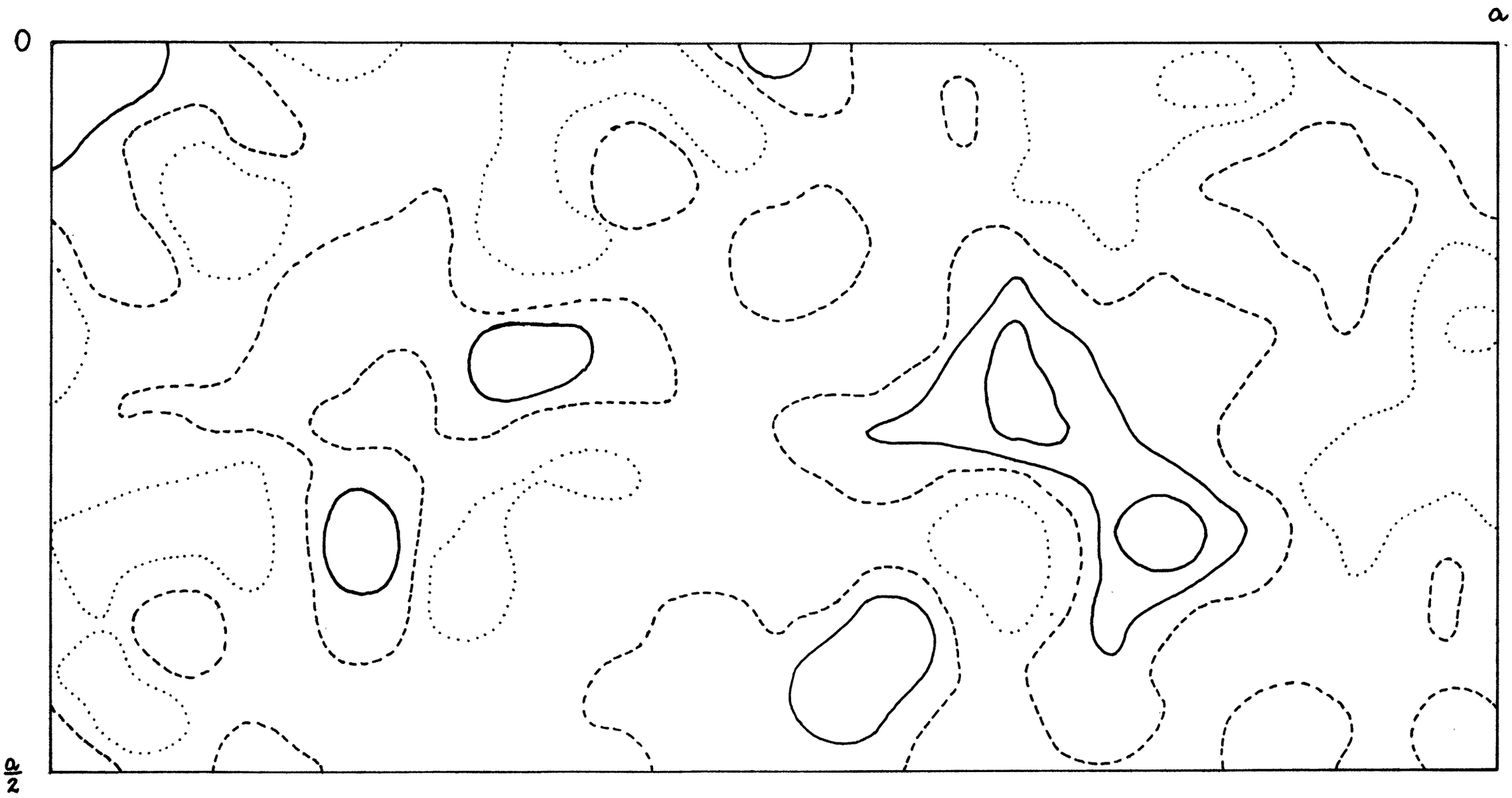
$\Delta\rho(\frac{8}{30}\ y\ z)$



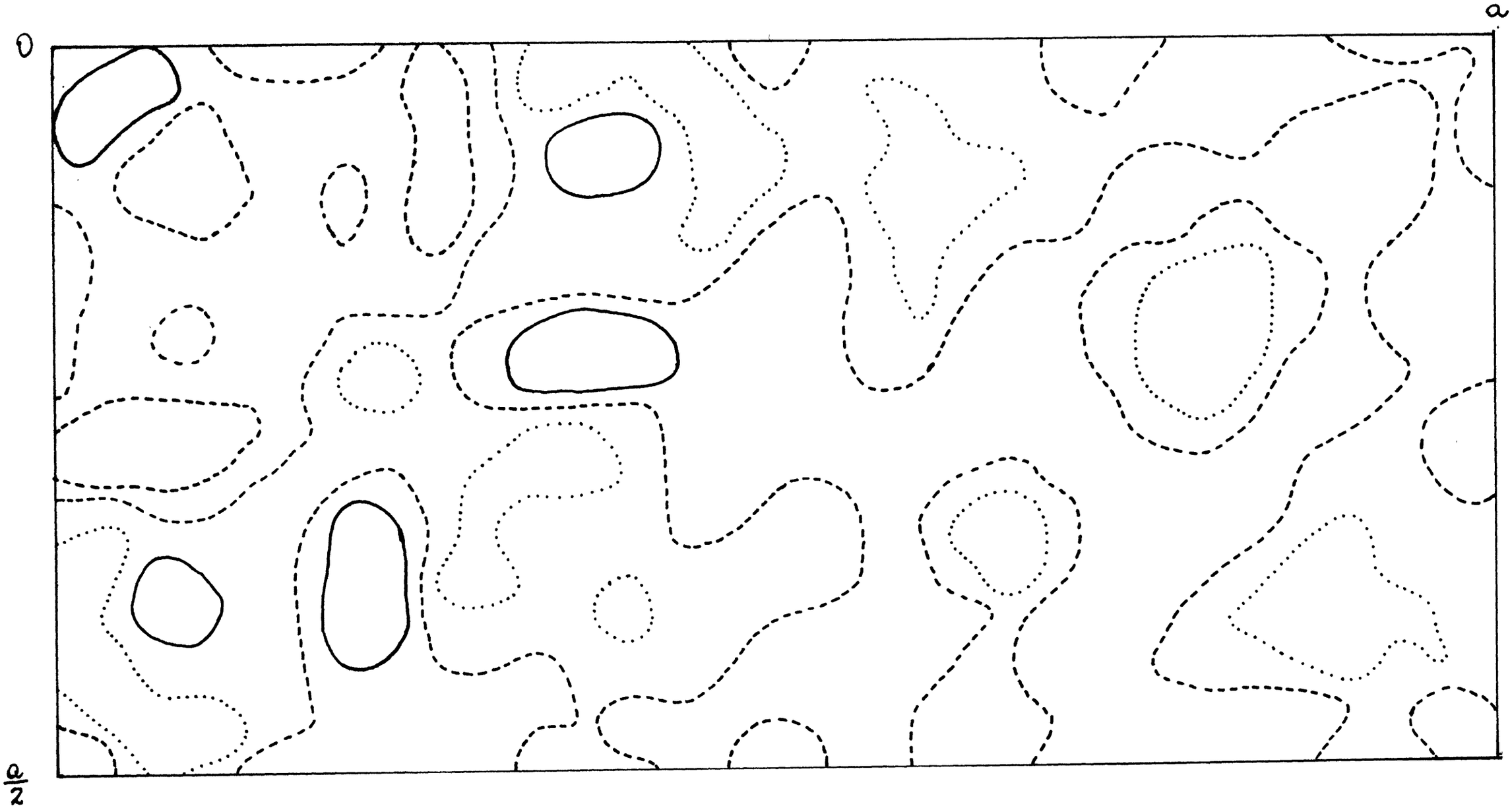
$\Delta\rho(\frac{9}{30}\ y\ z)$



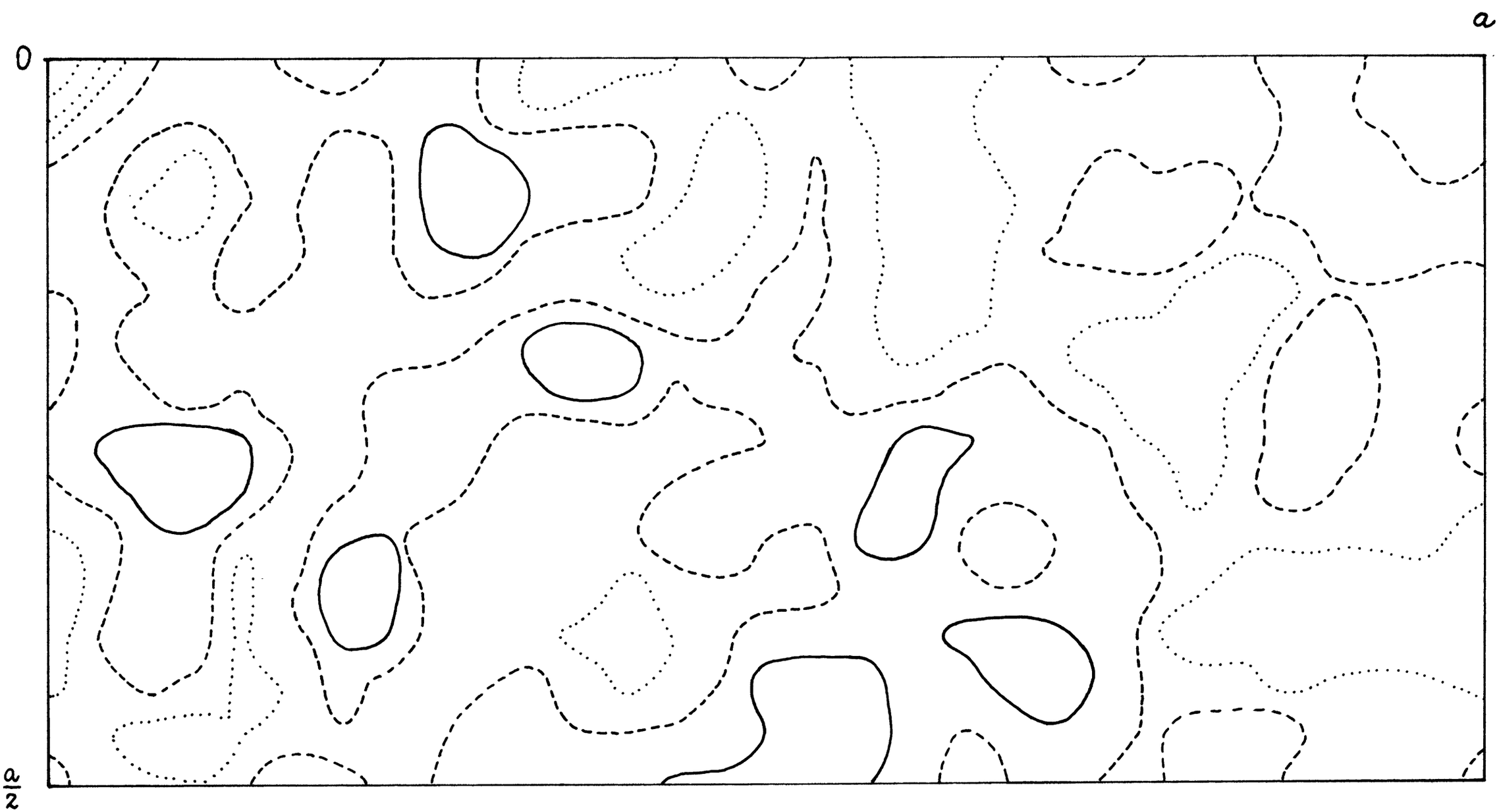
$\Delta\rho(\frac{10}{30}\ y\ z)$



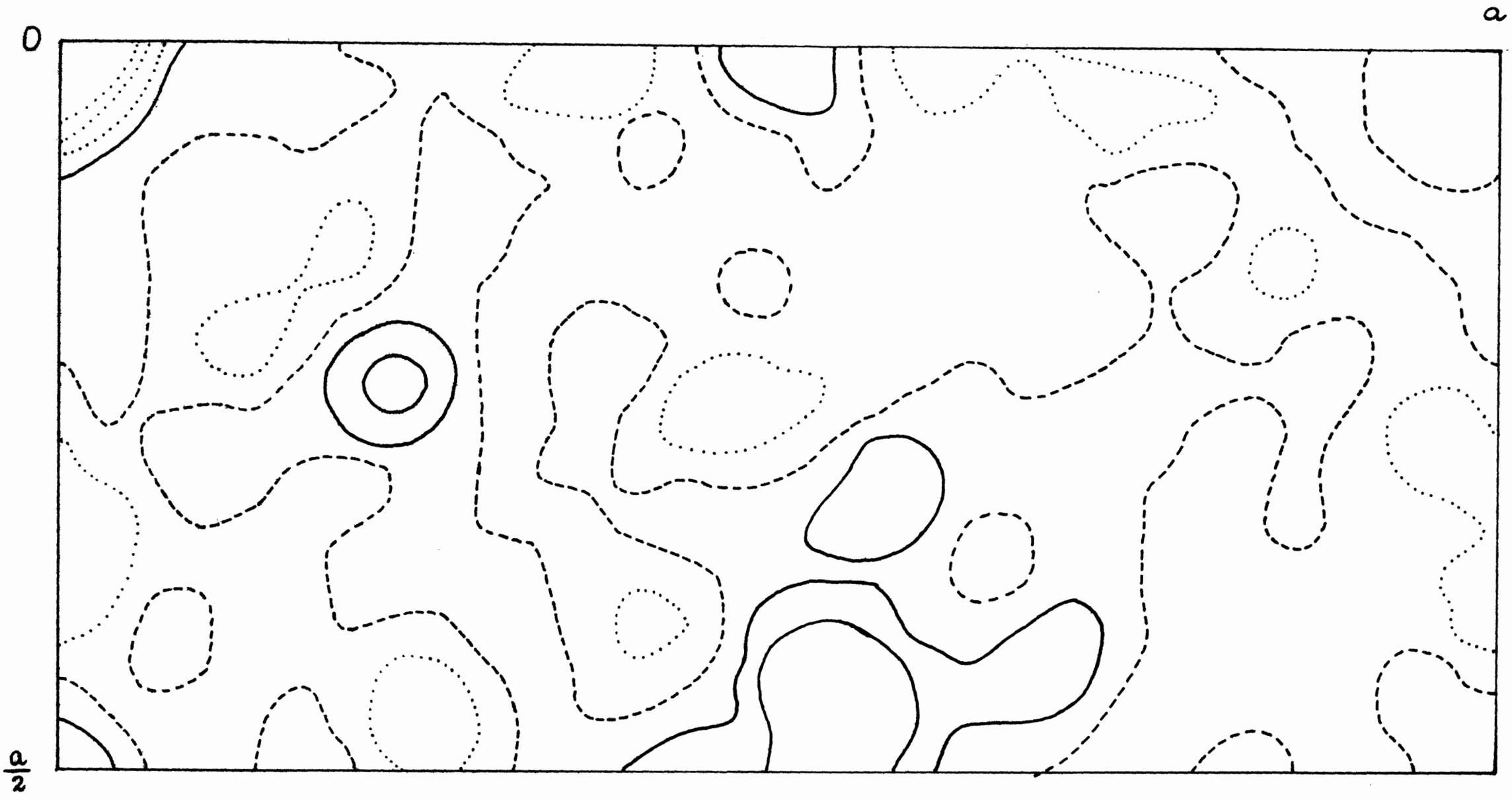
$\Delta\rho\left(\frac{11}{30}yz\right)$



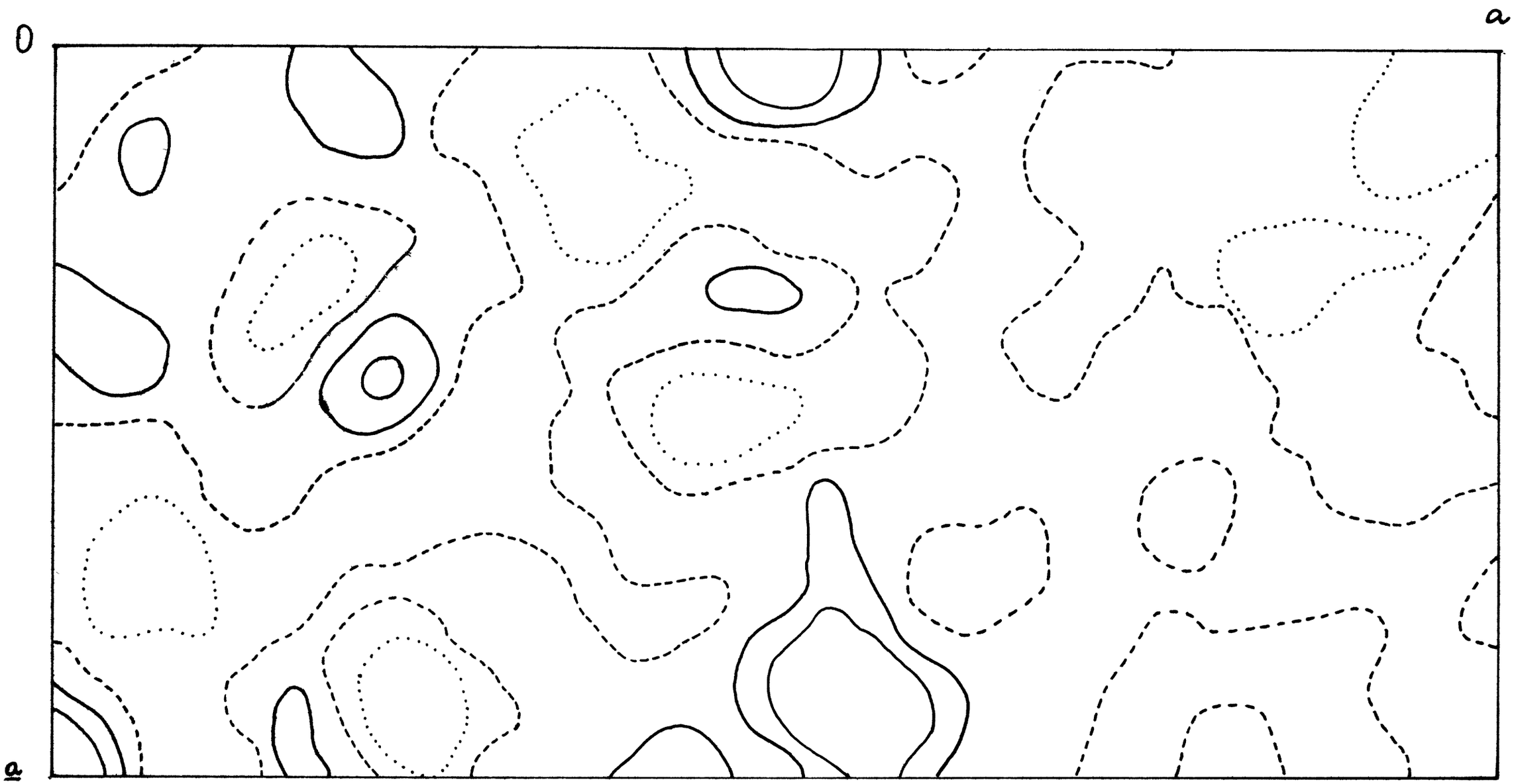
$\Delta\rho\left(\frac{12}{30}\,y\,z\right)$



$\Delta\rho(\frac{13}{30}yz)$



$\Delta\rho(\frac{114}{30}yz)$



$\Delta\rho(\frac{1}{2}\,y\,z)$